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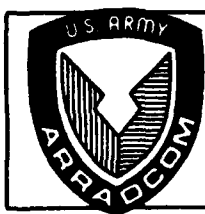
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TECHNICAL REPORT ARLCD-TR-81028

THE CHEMICAL CHARACTERIZATION OF POLLUTANTS IN WASTE WATER FROM VOLUNTEER ARMY AMMUNITION PLANT

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LARGE CALIBER
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report describes a characterization study of pollutants in waste water generated in manufacture of TNT (trinitrotoluene) at Volunteer Army Ammunition Plant in Tennessee. The major portion of the study was devoted to separation and identification of dissolved species and estimation of the concentrations of identified components. Inorganic pollutants were identified and estimated by spark source mass spectrometry and conventional wet chemical techniques. Organic pollutants were extracted from the waste waters

20. ABSTRACT (cont)

with methylene chloride and the extracts were characterized by means of
classical and multi-development thin-layer chromatography, gas chromatography,
infrared spectrophotometry, mass spectrometry, and tandem gas chromatography-
mass spectrometry. The waste waters were shown to be exceedingly complex mix-
tures of nitroaromatic compounds derived from the TNT manufacturing process and
heavy metal ions leached from the stainless steel reaction vessels. The
concentration levels of many of the inorganic pollutants in the waste waters
discharged into public waters exceeded the concentrations permitted by
federal and state environmental pollution standards.

ACKNOWLEDGMENT

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INTRODUCTION

Reliable analytical data on pollutants are indispensable to progress in environmental science and technology. These data are needed in the study of sources of contaminants and their impact on the environment, in the development and evaluation of abatement technologies, in setting standards for regulatory control, and in building predictive models.

Although considerable progress has been made in the recent past, the current analytical data for pollutant analysis are still inadequate to deal with complex environmental problems. The aim of this work is, therefore, to generate additional analytical data for the identification and quantification of pollutants in the wastewater effluents of Army Ammunition Plants as part of the Army's Pollution Abatement efforts.

This report describes a characterization study of wastewater samples emanating from the 2,4,6-trinitrotoluene (TNT) manufacturing process collected at various points at Volunteer Army Ammunition Plant (VAAP) in Tennessee. The major effort in this study was concentrated on separation and identification of dissolved organic species and estimation of the concentrations of identified species found in the collected condensate waters. Waste waters discharged into public waters were analyzed only for components specified in the federal and state environmental pollution standards.

EXPERIMENTAL

Sampling Techniques

The sampling technique developed by the Air and Stream Laboratory at VAAP was used for the collection of the water samples. A Technicon sampling device adapted with five spaghetti tubes through which waste water is drawn with a sigma pump, was employed over a 24 hour period for the generation of composite samples. Because of the low absorption of organic compounds on glass surfaces, glass was specified as the shipping and storage container for the sample waters. However, polyethylene containers were specified for samples intended for analysis for inorganic constituents.

Characterization of Organic Pollutants

Extraction of Organics

A 1 L volume of sample water was extracted with four successive 50 mL portions of methylene chloride ($MeCl_2$). In initial experiments extraction was found to be complete with the fifth 50 mL portion $MeCl_2$. Completeness of extraction was indicated by the absence of residue on evaporation of the solvent. The first four $MeCl_2$ extracts were combined and the solvent evaporated under a stream of dry air

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making sure to avoid condensation of moisture in the vessel containing the extract. The residue (extract) on evaporation of the solvent was characterized using the separation and identification techniques of thin layer chromatography (TLC), gas chromatography (GC), GC/mass spectrometry (GC/MS), and infrared (IR) spectrophotometry described below. If the quantity of the extract was insufficient for TLC, extraction of larger quantities of sample water was carried out.

Thin Layer Chromatography Separations

The complete resolution of a $MeCl_2$ extract was carried out in two phases.

First phase, classical TLC - Baker-flex silica gel 1B flexible sheets were cut into 2 cm x 6.5 cm strips for spotting. These strips were dried at 110°C for 30 minutes and stored in a desiccator. A strip was spotted with a $MeCl_2$ solution of the extract and devloped using a medium polar solvent mixture, e.g., 15:1 ethyl acetate in petroleum ether, contained in the CAMAG 3.5 x 5 x 9 cm TLC jar. If the migration distance and degree of resolution of the spot indicated poor separation, additional developments were carried out using freshly spotted TLC strips and other more or less polar solvent mixtures to achieve the maximum resolution of the original spot. Having determined the appropriate solvent mixture, an Analtec Uniplate, 20 x 20 cm, covered with silica gel GF, 250 or 1000 µ thick, which had been washed by developing it once with acetone until the solvent front migrated to the top of the plate and then air dried, was streaked with a solution of the extract. The choice of thickness of the silica gel layer was dictated by the concentration of the extract and the volume of sample water extracted. The streaked plate was placed in a large glass TLC chamber containing the appropriate solvent mixture, determined from spot TLC operations, for the classical TLC separation of large quantities of the extract. Visualization of colorless bands was made possible with a 254 nm UV radiation source. Since silica gel GF contains a fluorescent indicator and most nitro-compounds present in the sample waters are good UV absorbers, little difficulty was encountered in the detection of spot and band positions. Each detected band was carefully scraped from the developed plate and the silica gel eluted with acetone; the silica gel was removed by filtration. The acetone was removed from the eluate by evaporation under a stream of dry air at ambient temperature, leaving behind the separated band component.

Second phase, multi development (MD) TLC - A 2 x 6.5 cm TLC strip was spotted with an acetone or $MeCl_2$ solution of a separated band component. Selection of the solvent mixture for the initial development of the spotted strip was dictated by the R_f value of the original band. If the band had exhibited an R_f value greater than 0.5, a solvent mixture was selected having a polarity less than that used in the initial separation. A value less than 0.5 required the use of a more polar solvent. After the development of the spotted strip with the appropriate solvent, the developed strip was removed from the TLC jar. The solvent was allowed to evaporate from the strip and then the strip was reimmersed in the TLC jar containing the same solvent. This procedure was repeated several times until resolution of the initial spot had occurred or the spot was found to be unresolvable. A single development was considered as one pass when the solvent front had migrated to about 80% of the length of the TLC strip. As many as nine passes were made in some runs to achieve separation of the original spot into several spots. The nonresolution of

the original spot indicated that the band from phase one contained essentially one component, and no further resolution of the band was necessary. All bands from phase one were treated similarly. The MDTLC procedure developed by spotting the small TLC strips was applied to the remaining portion of the separated component using an acetone washed Analtec Uniplate, 20 x 20 cm. After the final pass, the new bands were scraped off the plate and the components isolated by elution of the silica gel with acetone or $MeCl_2$. The isolated components from each new band were subjected again to the spot MDTLC procedure already described. This operation was repeated for subsequent new bands until a complete resolution of the $MeCl_2$ extract was achieved.

The isolated components from phase 2 were subjected to MS and IR examination for possible identification. Where sufficient material was isolated, other identification techniques were also used for the identification of the isolated components.

Gas Chromatography Separations

Separations. A Varian model 1840 gas chromatograph equipped with flame ionization (FI) and thermal conductivity detectors (TCD) was used. A stainless steel column, 9 ft x 1/8 in. was packed with a 4% Dexsil 300 on Analab ABS support. The temperature was programmed from 100° to 250°C at 8°C per minute. Helium was used as the carrier gas, with a flow velocity of 32 mL per minute. The volume of the $MeCl_2$ solution of the extract injected was dependent on the sensitivity setting used. Usually the sensitivity was set at the highest value, 4×10^{-11} amperes full scale (AFS). A lower sensitivity setting was used when background noise levels were encountered.

The flame ionization detector (FID) was used to obtain a chromatogram at the highest sensitivity setting possible in order to establish the greatest number of detectable peaks for mass spectrometric examination. However, in the collection of effluent from the exit port of the GC, the TCD was utilized since the FID decomposes the separated component. Each component was collected in a small glass cup about 5 to 6 mm deep and 4 mm in diameter. The cup was placed over the exit port, making sure it was not heated by the exit tube for condensation of the vapor on the cold inner surface of the cup. Repeated injections of the $MeCl_2$ extract resulted in the collection of significant amounts of the separated components for IR spectrophotometric or mass spectrometric examination.

Spiking. Spiking in GC is the technique wherein a comparatively large quantity of a compound suspected to be a component of an unknown mixture is added to the mixture and its chromatogram is redetermined. A large increase in the size of the suspect peak (a spike) strongly indicates the presence of the added compound in the original mixture.

Quantitation. The internal standard procedure was used for the condensate water sample no. 3 (CW3) components p-nitrotoluene being used as the standard. For the remaining samples, the normalization procedure was used; that is, the sum of all peak areas is divided into the area of each peak to give the percentage of each component. In this latter procedure, it is assumed that the chromatogram obtained is representative of all the components in the $MeCl_2$ extract.

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Infrared Spectrophotometry

The TLC or GC separated components were mixed with IR quality potassium bromide to form micro pellets. A Perkin-Elmer model 621 IR spectrophotometer with a slave recorder was used to obtain spectra of the pellets between 4000 cm^{-1} and 200 cm^{-1}. Identifications were made by comparison of the IR spectra of the unknowns with standard reference spectra.

Mass Spectrometry

Mass spectrometry was employed to identify components isolated by both TLC and GC when the amount of material collected was not sufficient for successful identification by micro-IR techniques. A DuPont model 21-492 MS employing electron impact ionization at 70 electron volts was used. The samples were introduced into the ion source of the spectrometer via the solid probe. The ion source was maintained at 250°C. The temperature of the solid probe was varied from 50°C to 210°C, depending on the volatility of the sample. Mass scanning was done at 10 seconds/ decade of mass units at a sensitivity setting of six and a current amplifier gain of 10^7. Mass data were either obtained manually or acquired and stored by an Associated Electrical Industries (AEI) DS-30 computer system with an off-line mass identification software program.

Gas Chromatography/Mass Spectrometry

The GC/MS consists of a Varian 2700 series GC with an FID interfaced to the DuPont model 21-492 MS. The interface essentially consists of a column effluent splitter and an all glass jet separator. Although a different column (SE-30) was used, the GC parameters were generally similar to those used with the Varian model 1840. A concentrated $MeCl_2$ extract of the sample water was injected into the GC in 5 mL portions and separated on the SE-30 column. The initial column temperature was 100°C and the final 225°C, programmed at 6°C per minute for the CW3, and 4°C per minute for the red water condensate (RWC) 4/14/77 extracts. Mass data were acquired and stored by an AEI DS-30 system with an off-line mass identification software program. Repetitive scanning by the MS was done during the GC analysis either at 4 seconds/decade of mass units or 2 seconds/decade depending on the calibration and mass identification routines.

Three basic shortcomings were initially observed with our instrumentation. One was the poor conductance of the jet separator resulting in a delayed response to the eluted GC peaks. This was corrected by dismantling and cleaning the GC line and by installing a new jet separator. The $MeCl_2$ extract of RWC 4/17/77 was analyzed after this modification was made and, therefore, reflects an improvement over the results obtained initially in the CW3 $MeCl_2$ extract analysis. The second problem pertained to the scan frequency. At 4 and 2 seconds/decade, the number of scans obtained per minute were only 4 and 7, respectively. This was due to a fixed turn-around time (interscan dead time) of 4 seconds. It is essential to get more scans per minute to monitor narrow GC peaks. The circuits were modified to cut the dead

time down to about 1 second. The third problem appeared to be with the MS computer interface, which failed mass identification at 2 or 1 second scanning speeds. Fast scanning speeds are essential to get high quality reconstructed chromatograms and individual mass scans which can differentiate spectra of isomeric compounds. It was possible to obtain some satisfactory calibrations at 2 seconds/decade, which enabled the analysis of RWC 4/17/77. However, efforts were made to improve the interface parameters and get reliable calibrations at 1 second/decade mass scanning speed.

Analysis of Volatile Components by High Performance Liquid Chromatography

Fractionation

About 40 mL of CW3, as received, was placed in the 100 cm^3 round bottom flask portion of the vacuum manifold illustrated in figure 1. The sample was degassed twice at $-78°C$, using a dry ice trichloroethylene bath. After degassing, the temperature of the condensate water was raised to $-5°C$ with an ice salt bath and the volatiles distilled into the cylindrical container on the manifold, which was cooled to $-78°C$ with the dry ice trichloroethylene bath. In this manner approximately 2 cm^3 of aqueous sample was fractionated from the condensate water. The above fractionating procedure was repeated with 40 mL of CW3 after adjusting its pH to 2 with sulfuric acid, and with 40 mL of CW3 after adjusting its pH to 12 with sodium hydroxide. The three distilled samples were reserved for further analysis by liquid chromatography (LC).

Liquid Chromatography

A reversed phase isochratic LC procedure for the analysis of the aforementioned fractionated samples of condensate was developed. The experimental conditions used for analysis were a 30 mL sample injection, a mobile phase consisting of 15% acetonitrile and 85% water, oven temperature of 55°C, flow rate of 0.7 mL/min, and ultraviolet (UV) detection of the resolved components at 254 nm. The desirable feature of this analytical procedure is that the aqueous sample may be introduced into the chromatograph directly.

Characterization of Inorganic Pollutants

Inorganic elements were determined by spark source MS analysis. An AEI model 702 MS equipped with electrical detection in the peak switch mode was used for quantitative analysis. The magnet scan decay mode was used for semi-quantitative analysis. All elements present in concentrations as low as 10 parts per billion were determined.

For magnetic decay scan mode MS, 5 mL of the filtered water was pipetted into a 20 mL platinum dish. Ten mg of yttrium (Y) (as chloride), 50 mL of ethanol, 50 mL of ethyl ether, and 100 mg of spectrographically pure graphite were then added in
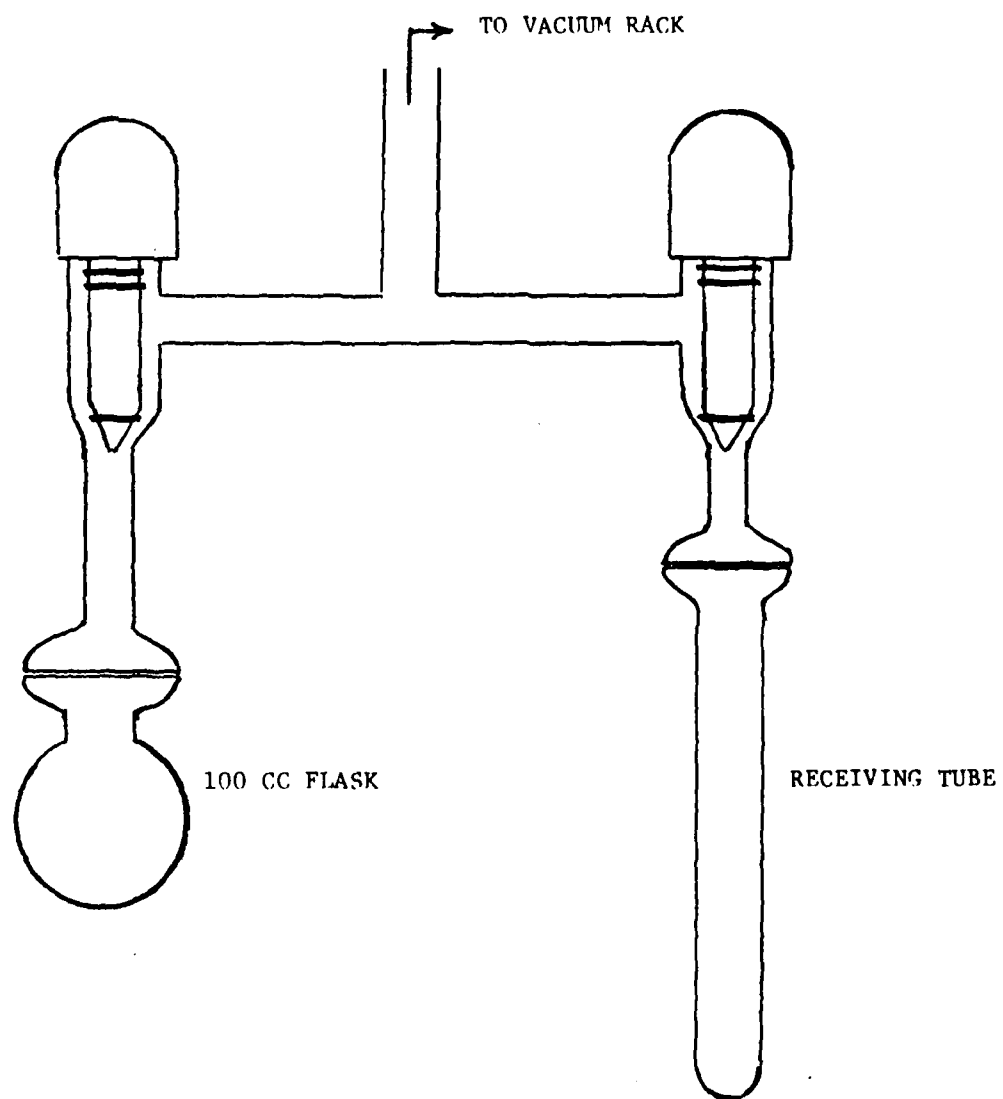
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TO VACUUM RACK

100 CC FLASK

RECEIVING TUBE

Figure 1. Vacuum fractionation apparatus

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the sequence mentioned. The mixture was evaporated to dryness on a steam bath and heated to 550°C in a muffle furnace to destroy any organic material. The mixture was transferred to a 5 mL tungsten carbide vial containing tungsten carbide balls and was vibrated for 10 minutes in a dental amalgamator. The powder was then transferred via a sheet of glassine weighing paper to a polyethylene plug having three pre-tapped holes 2 mm x 8 mm. The plug was placed in an AEI die and pressed isostatically at 20 tons for 10 minutes. Two of the three electrodes prepared by this procedure were mounted in the spectrometer source so that they were 4 mm from the accelerating plate with 2 mm overlap and a spark gap of 1 mm.

For peak switch electrical analysis, 10 mg of each element found in the magnetic scan are added in solution as the chloride to 100 mg of graphite. Data are obtained by manually switching the voltage to each element of interest and measuring the number of counts equivalent to 0.1 nanocoulombs of charge. Standard electrodes are analyzed in the same fashion. Calculations are made from ratio of the counts of the sample to that of the standard which contains 100 ppm of each element. The operating conditions are listed in table 1.

Table 1. Spark source mass spectrometer operating parameters

Charge collection	0.1 nanocoulombs
Spark gap voltage	3
Pulse repetition rate	300 pulses/second
Pulse duration	100 micro-second
Prespark time	5 minutes
Vacuum system:	
Magnetic analyzer	1×10^{-8} torr
Electrostatic analyzer	1×10^{-8} torr
Source	5×10^{-7} torr using dual pumping

Flameless atomic absorption (AA) spectrometric analysis was also used to determine inorganic components. A Perkin Elmer model 306 AA spectrometer, equipped with a model 2100 graphite furnace was used to check the spark source data, and also used for the determination of the alkali and alkaline earth elements, which are not easily determined by spark source MS. In addition, silicon, aluminum, and magnesium were determined whenever the concentrations were appropriate for AA.

Samples for AA analysis were acidified and pipetted into the furnace. Usually, 100 µL of the sample was used, but if the concentration of the element was too low or detection limits too high, additional sample was added. The water was evaporated at 110°C and the sample was washed and atomized at the appropriate temperature for each element for about 7 seconds. Two reference standards with concentrations higher and lower than that of the unknown sample are analyzed in the same fashion, and the concentration of the unknown is calculated by simple proportion.

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Standard wet chemical analyses were used for identification and quantitation of anions (refs 4,5).

RESULTS AND DISCUSSION

The major portion of this characterization study was devoted to separation and identification of dissolved species in the sample waters and estimation of concentrations of the identified components. Some effort was devoted to development and/or establishment of methods of analysis. It is believed that in future studies a greater effort should be devoted to the latter. The characterization study was divided into organic and inorganic phases. Samples, collected by the technique described in the Experimental section, were taken at various points at the VAAP (fig. 2). A summary of the 24 hour composite water samples received is given in table 2. Of the samples collected, CW3, RWC 4/14/77, and water sludge from pond 5 were specifically designated for organic analysis with some inorganic analyses when required. The remaining samples were subjected to inorganic analysis with very little or no organic analysis. The results of the inorganic analyses are shown in tables 3 and 4.

Preliminary Examination of Sample Waters

Sample CW3 was received as clear, pale yellow-colored water with a pH of 6.2, containing 49 ppm dissolved solids. Elemental and anionic analysis of the water solubles, shown in column 5 of table 3, indicated that nitrate, nitrite, silica and sulfate, and bicarbonate were the major anions, and sodium were the major cation elements present. The MeCl$_2$ extractables from the as received sample totaled 19.2 ppm. Acidification of the aqueous phase of the first extraction added an additional 1.2 ppm to these MeCl$_2$ extractables. Red water condensate 4/17/77 on the other hand was received as a dark, red-colored water with a pH of 7.3, containing 1,390 ppm of water soluble solids and 2.7 ppm of MeCl$_2$ extractable materials. Thermogravimetric analysis of the water soluble solids showed a 26% loss in weight on heating to 800°C. Infrared spectrophotometry revealed the presence of sulfate, nitrate, and nitrite. Atomic absorption showed an abnormal amount of sodium. Since this sample was reported at VAAP as "atypical" condensate water, additional characterization by inorganic analyses was not carried out.

The water and sludge from pond 5 were received in separate shipments. The water, straw yellow in color and turbid in appearance, contained 335 ppm of water soluble solids, and 1.8 ppm of MeCl$_2$ extractable materials. An air-dried sample of the sludge contained 1,480 ppm of MeCl$_2$ extractable material. Preliminary TLC separation of this extract showed it to be predominantly nonpolar material. Further extraction of the MeCl$_2$ extract with petroleum ether revealed that this nonpolar material made up 62% of the MeCl$_2$ extract (918 ppm of the dried sludge). Infrared spectrophotometry indicated it to be a hydrocarbon wax or grease.

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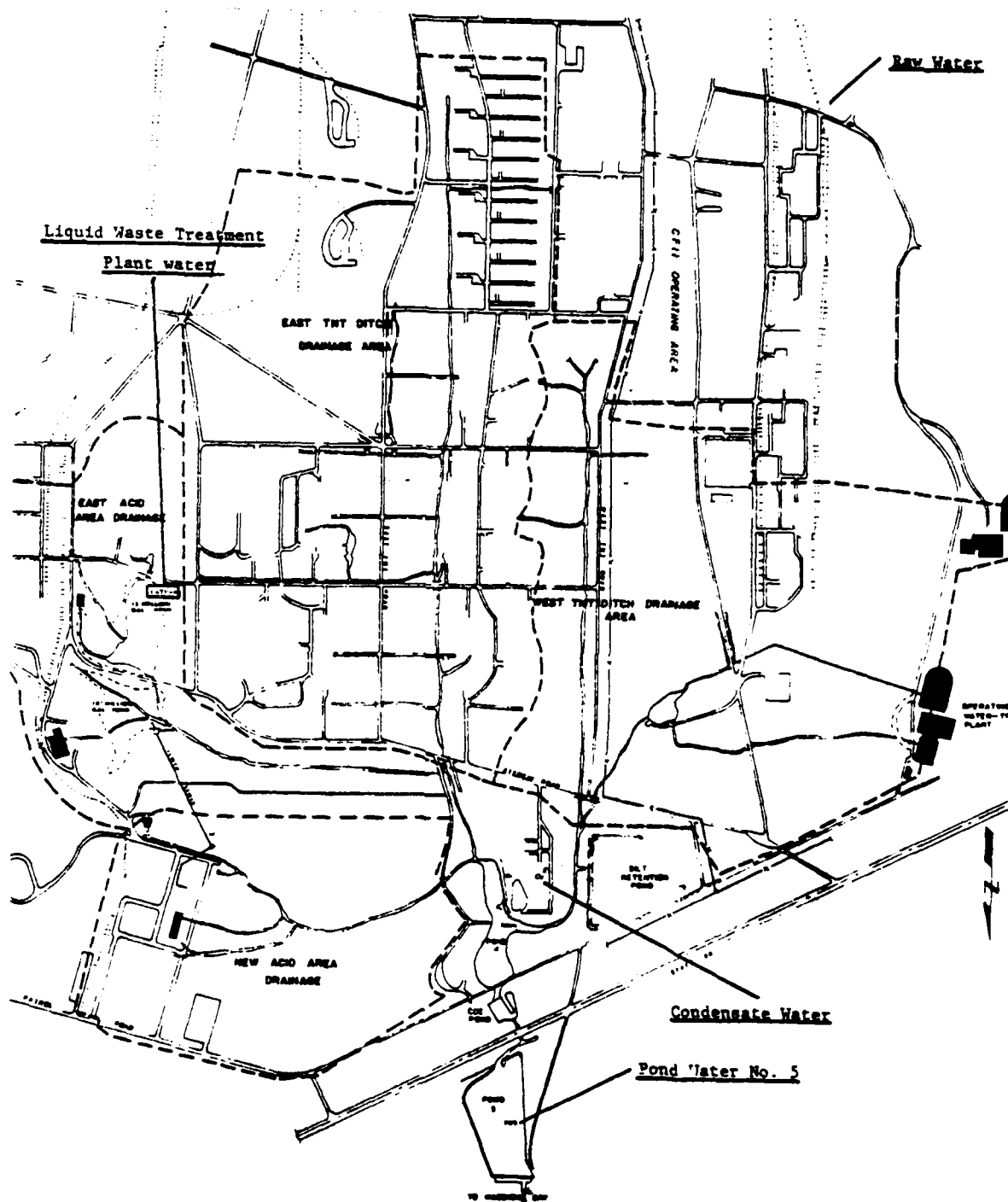
Figure 2. Map of VAAP showing water sampling points

Table 2. Description of 24 hour composite water samples collected at VAAP

Sample designation	Container vol/composition	Source	Tubing composition
CW-3 4/30/76	5 gal/glass	condensate water	glass
CW-3 4/30/76	1 gal/plastic	condensate water	plastic
CW-1 12/10/75	1 gal/plastic	condensate water	plastic
LWTPW-1 10/10/75	1 gal/plastic	liquid waste treatment plant water (LWTPW)	plastic
CW-4 4/30/76	1 gal/plastic	condensate water	plastic
SW 12/25/76	1 gal/plastic	service water (filtered)	plastic
LWTPW-2 4/30/76	1 gal/plastic	liquid waste treatment plant water (LWTPW)	plastic
RWC 4/14/77	20 gal/glass/ plastic*	red water condensate	glass
PW5	20 gal/glass/ plastic*	pond water	glass
Sludge	1 gal/glass*	pond water	glass
Discharge water 4/30/76	1 gal/plastic	water discharged into public waters	glass
Discharge water 8/17/76	1 gal/plastic	water dischared into public waters	glass
Discharge water (composite) 8/20/76-8/23/76	1 gal/plastic	water discharged into public waters	glass
Discharge water 9/03/76	1 gal/plastic	water discharged into public waters	glass
Discharge water 9/25/76	1 gal/plastic	water discharged into public waters	glass

*Waters received in glass bottles were quickly transferred to plastic containers.

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Table 3. Analyses of intake, condensate, and liquid waste treatment waters at VAAP

Determination	Svc wtr SW 12/20/76	On site condensate waters				On site liquid waste treatment plant	
		CW1 12/10/75	CW2 4/30/76	CW3 4/30/76	CW4 4/30/76	LWTPW-1 12/10/75	LWTPW-1 4/30/76
	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Sodium	36.9	20.0	0.90	1.10	1.07	66.0	95.6
Potassium	0.64	0.51	0.78	0.07	0.12	5.5	0.78
Calcium	26.0	55.0	2.17	0.02	0.06	187.0	95.0
Magnesium	1.10	2.10	0.05	0.004	0.03	2.0	1.9
Aluminum	0.49	0.47	0.03	0.007	1.60	1.3	1.4
Iron	0.20	0.50	0.83	0.04	0.05	2.0	0.69
Silicon	0.70	1.52	4.20	1.60	3.2	12.7	9.70
Phosphorous	0.21	0.17	0.14	0.01	0.07	0.56	0.02
Sulfur	23.7	850	4.50	1.9	2.6	395	19.0
Zinc	0.50	0.62	0.15	0.01	0.004	0.90	0.05
Cobalt	0.65	0.65	N.D.	0.01	N.D.	0.65	N.D.
Boron	0.31	0.023	N.D.	0.01	0.020	0.23	N.D.
Nitrogen	N.D.[a]	24	3.0	20.0	15.0	20	109.
Lead	N.D.	0.33	0.03	N.D.	N.D.	0.53	0.13
Thallium	N.D.	0.21	N.D.	N.D.	N.D.	N.D.	N.D.
Tungsten	N.D.	0.094[b]	N.D.	N.D.	N.D.	N.D.	N.D.
Bromine	N.D.	0.009	0.03	0.02	N.D.	N.D.	0.04
Copper	0.01	0.13	0.06	N.D.	N.D.	0.07	0.03
Nickel	0.03	0.06	0.35	0.005	N.D.	0.48	0.08
Chromium	N.D.	0.10	0.04	N.D.	N.D.	0.12	0.05
Vanadium	N.D.	0.002	0.02	N.D.	N.D.	N.D.	0.012
Manganese	N.D.	0.06	0.04	N.D.	N.D.	0.12	0.22
Strontium	N.D.	N.D.	N.D.	N.D.	N.D.	0.22	0.15
Arsenic	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.70
Cesium	N.D.	N.D.	0.04	N.D.	0.70	N.D.	0.04
Barium	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.28
Cerium	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.023
Lanthanum	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0032
pH	8.3	6.4	7.22	6.20	6.20	1.9	3.9
Bicarbonate	96	12.0	24.8	8.70	8.0	Nil	Nil
Chloride	9.0	3.0	N.D.	N.D.	N.D.	33.0	29.9
Nitrate	1.4	14.0	4.2	10.3	4.6	9.0	454
Nitrite	0.64	106.0	7.3	15.7	6.3	0.82	1.28
Sulfate	43.5	3590	N.D.	N.D.	N.D.	745	56.6
Phenols	N.D.	N.D.	3.4	0.024	2.1	0.046	0.08
Kjeldahl N	N.D.	268	38.8	1.9	20.5	1.30	0.28
Dis solids	171	12000	43.5	49.0	40.0	3230	1060
Dis solids/ acetone	N.D.	4270	14.5	25.0	21.0	2380	749

[a] N.D. = not detected
[b] Contaminant

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Table 4. Spark source mass spectrometric and classical chemical analyses of discharged waters

Determination	4/30/76	8/17/76	3 day composite 8/20/76- 8/23/76	9/03/76	9/25/76
	ppm	ppm	ppm	ppm	ppm
Sodium	12.2	138.	55.2	32.3	34.9
Potassium	4.2	0.82	0.73	0.43	0.72
Calcium	0.52	47.5	430.	69.5	47.5
Zinc	0.04	0.13	0.05	0.20	0.13
Iron	0.27	0.03	.01	0.03	0.02
Magnesium	1.11	0.93	0.94	0.87	0.79
Copper	0.01	0.22	0.16	0.09	0.05
Manganese	0.02	0.02	0.30	0.18	0.05
Chromium	0.09	0.16	0.10	0.11	0.12
Lead	0.002	0.01	0.007	0.004	0.03
Silicon	16.6	2.3	1.90	3.3	3.4
Phorsporus	0.007	0.10	0.02	0.003	0.08
Nickel	0.12	0.11	0.22	0.13	0.12
Vanadium	.009	0.17	0.15	0.034	0.08
Bromine	0.06	0.18	0.99	0.06	0.29
Arsenic	0.09	0.07	0.08	0.09	0.03
Barium	0.017	0.05	0.02	0.02	0.06
Cesium	0.27	0.02	0.06	0.01	0.07
Sulfur	47.5	42.7	48.0	43.0	38.8
Nitrogen (total)	>>11.0	>>10.0	>>50.0	>>10.	>>10.
Strontium	N.D.	0.13	0.12	0.08	0.17
Cerium	N.D.	N.D.	N.D.	N.D.	N.D.
Lanthanum	N.D.	N.D.	N.D.	N.D.	N.D.
Aluminum	0.075	0.29	0.03	0.06	0.15
Dis solids[a]	367.	552.	1997.	410.	334.
Dis solids/ HCl added[b]	485.	605.	2071.	888.	330.
pH	7.90	8.18	7.32	7.60	7.75
$SO_4^=$	63.6	204.	995.	151.	101.
Cl^-	13.5	71.3	187.	87.9	17.9
NO_2^-	1.56	N.D.	N.D.	6.8	N.D.
NO_3	21.0	27.0	295.	4.6	62.
Phenol	0.04	0.62	0.86	N.D.	1.95
HCO_3^-	52.4	134.0	28.6	42.0	71.8
Organic N	1.12	0.56	0.70	0.84	1.12

[a]Dissolved solids
[b]Dissolved solids after the addition of hydrochloric dried (HCl) to the original water.

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Organic Phase

The analysis essentially consisted of concentration of the organics by solvent extraction, resolution of the extract into its components by chromatography, and identification of the separated components. An estimation of quantities of components separated by GC was made when the extract lended itself to the technique. Limited attention was paid to the development of procedures for the analysis of volatile components that escaped detection by the procedures used. Very little attention, if any, was paid to those components that remained in the aqueous phase after the solvent extraction of the sample and to pre-extracts of acidified aqueous phase from an initial $MeCl_2$ extract.

Extraction of Organics

Most water analyses for trace organics require prior separation of the components from the aqueous phase. The most widely used separation procedure is liquid-liquid extraction with an organic solvent. Of the more common solvents ordinarily used for extracting organic compounds, viz., ether, benzene, and $MeCl_2$ was preferred on the basis of its chemical stability, extractive ability, and ease of evaporation.

An estimation of the extraction efficiency of $MeCl_2$ in a liquid-liquid extraction system was made. A sample of waste water was freeze-dried to obtain a solid residue. This residue was then extracted with $MeCl_2$ and a weight of the solid extract was obtained. The weight of the $MeCl_2$ solubles obtained by this procedure was equal to the weight of the $MeCl_2$ solubles obtained by extracting an equal volume of waste water directly with $MeCl_2$, indicating an acceptable direct liquid-liquid extraction efficiency, at least with respect to the $MeCl_2$ solubles in the sample waters.

A measure of the precision that can be expected in the various $MeCl_2$ extraction procedures employed in this work is shown in table 5. The precision is considered acceptable. The direct liquid-liquid extraction of CW3 exhibits a standard deviation of 1.03, the liquid-liquid extraction of the acidified aqueous phase resulting from the initial extraction exhibits a standard deviation of 0.2, and the determination of the residue remaining after the evaporation of the aqueous phase resulting from the second extraction exhibits a standard deviation of 3.19. The concentrations shown in the table were obtained by extracting six, 1 L batches of CW3 with $MeCl_2$, evaporating the $MeCl_2$, and weighing the solid extracts. The solid extracts obtained from the first extraction were combined for TLC examination as described below.

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Table 5. Precision of procedures used for the determination of MeCl$_2$ extracts and aqueous phase solids

		Concentration of extract in CW3						Std	
	Detn. no.	1	2	3	4	5	6	avg	dev
1st MeCl$_2$ extract of "as received" CW3 ppm		19.8	18.6	20.3	18.9	17.9	20.6	19.4	1.03
2nd MeCl$_2$ extract after acidification (following 1st extraction) ppm		1.4	1.8	1.6				1.6	0.2
Solids obtained on evaporation of aqueous phase after 2nd MeCl$_2$ extraction, ppm		64.8	70.0	68.0	62.2	63.7		65.7	3.19

Thin Layer Chromatography

In carrying out the characterization of MeCl$_2$ extractable organics in the sample waters, particular attention was paid to separation techniques that did not alter the integrity of the organics during the separation. This was considered critical because of the thermal instability of some of the compounds. Classical TLC and MDTLC techniques were selected on this basis, and because of their capability for resolving complex mixtures more completely than other available techniques. Stahl (ref 1) has described the MDTLC technique and Jupille (ref 2) covers this technique in his review of high performance TLC. A disadvantage of the MDTLC technique is the length of time required for achieving the optimum separation.

The complete resolution of a MeCl$_2$ extract was carried out in two phases, as described in the Experimental section. Spot TLC, selected for the purpose of using a minimal amount of the extract, was applied in both phases for the selection of developing solvents. Classical TLC (first phase) was used to separate the extract into major TLC bands and MDTLC (second phase) to further resolve each separated major band until complete resolution of the extract was achieved.

Initially, the TLC analysis of the MeCl$_2$ extract of CW3 resulted in the detection of at least 17 compounds. Figure 3 shows, schematically, how this was accomplished. Extraction of 1.25 L of CW3 with MeCl$_2$ yielded an aqueous phase and an organic phase; the MeCl$_2$ solubles. The main organic extract, MSR-1, was subjected to a series of chromatographic separations. The first classical separation yielded 10 bands, which were grouped into six zones, each zone containing one or more bands, depending on the degree of separation of the bands. The second separa-
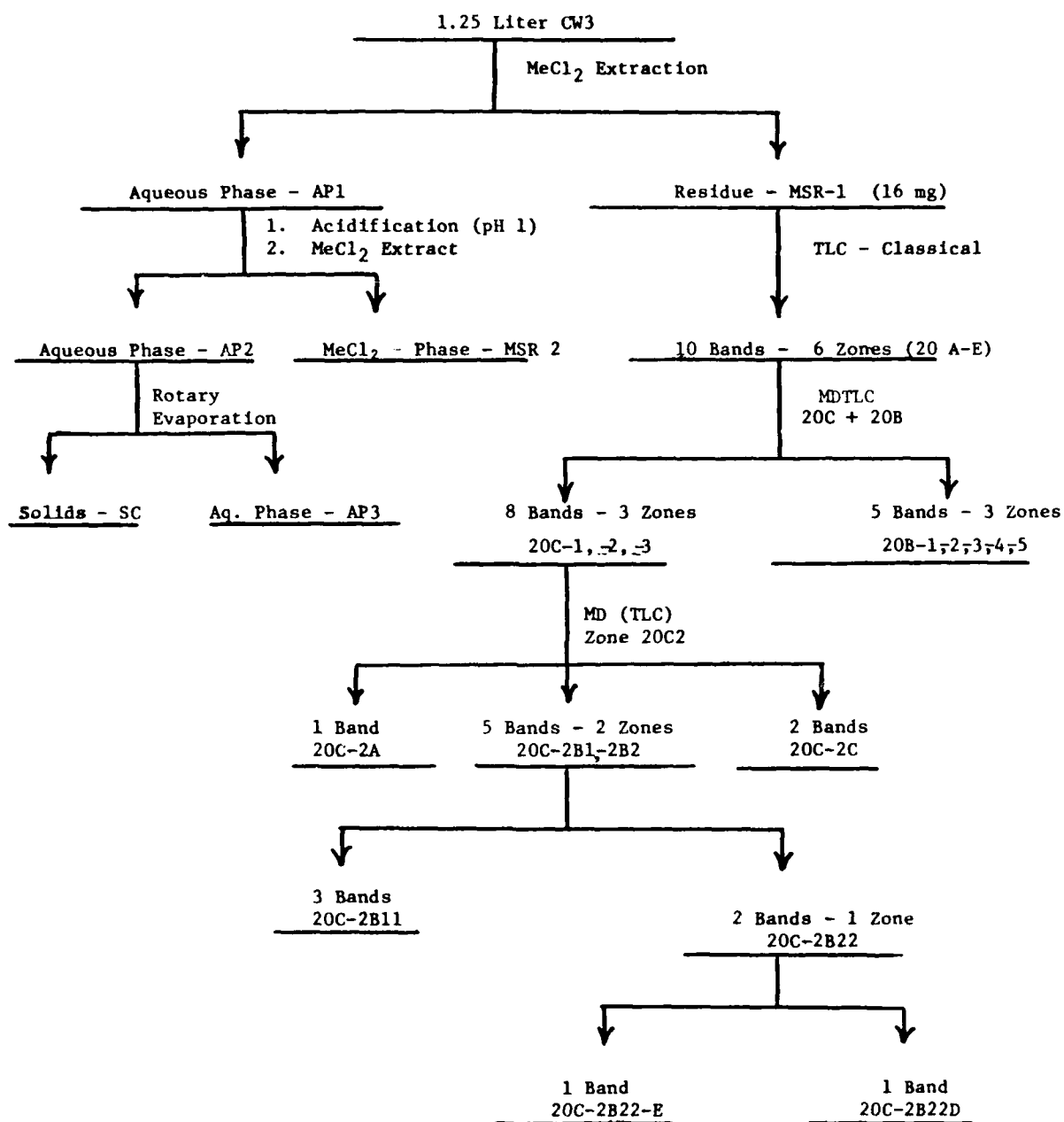
14

Figure 3. Flow diagram of MDTLC of CW3 in MeCl$_2$ extract

tion involved MDTLC of the zones containing poorly resolved bands, which eventually yielded additional well resolved bands. The procedure was continued until the separated bands were found to contain only one component. For example, zone 20C, which contained three poorly resolved bands, eventually yielded eight bands. A continuation of the MD of all six zones initially separated by classical TLC eventually resulted in the separation of 30 components. In many instances, the quantity of the separated component was insufficient for its identification. As a consequence, six 1 L batches of CW3 were extracted with $MeCl_2$ and each extract subjected to the separation scheme as shown in figure 4. Components having identical retention times were combined to yield a larger quantity of the separated components. For example, XB2 is a combination of separated components obtained from all six 1 L batches of CW3. Fraction CAM is a combination of the $MeCl_2$ extracts of the acidified aqueous phase; CAM was subjected to MDTLC for resolution of the trace components. Fraction CRA is the combined residues from the acidified aqueous phase, and CBS is a combination of solids insoluble in both $MeCl_2$ and the acidified aqueous phase.

Table 6 gives the results of the attempt to identify each TLC band. All bands, except XE and those obtained from extracts of the acidified sample, were examined. XE was not examined because it contained very highly polar compounds, difficult to solvent extract from the silica gel. The compounds recovered from the TLC bands were examined by micro-IR spectrophotometry when a sufficient quantity of the separated compound was recovered. Mass spectrometry was used as an adjunct technique when the micro-IR was not capable of identifying the separated material. The micro-IR was able to identify, through reference spectra, the components in TLC bands XB1, XB2, XC2A3, XD2, and XD3, because enough material was recovered. The bands XD2 and XD3 oddly enough, turned out to be identical, a phenomena occasionally observed for other separations. The only explanation that can be offered at this time for the occurrence of a component occupying two different sites on a TLC plate is a combination of (1) mechanical movement of the solute and (2) movement of the solute due to interactive force between the absorbent and mobile phase. Under ideal TLC conditions the latter is the only control for the movement of the solute across the TLC plate.

The micro-IR technique requires a minimum of 50 µg in order to obtain a well defined spectrum for identification purposes. On the other hand, the minimum that can be visually detected with MDTLC is 0.015 mg for spot TLC, and 0.15 µg for the band mode. The dimensions of the visualized band being 18 cm long x 10 mm wide with a 250 µ thick silica gel layer. The quantities denote a potential detection level of two parts per trillion for spot, and 20 parts per trillion for band mode, with respect to original samples. However, the actual detection levels were dictated by the identification technique, and not by the separation technique. With respect to the micro-IR technique, the minimum detection level was calculated to be 50 parts per billion for 6 L of CW3. However, we found this level to be even higher because of mechanical losses encountered during the recovery of the separated material and because of intrinsic characteristics of MDTLC, e.g., restreaking of recovered components, band broadening, efficiency of solvents to extract the separated components from silica gel, etc. Considering the number of separations and recoveries of separated components carried out during this characterization, it was felt a 10 to 30% recovery was reasonable. Using the lower figure, the quantity of material in a silica gel band would have to be equal to 50 µg for identification by micro-IR. The combined IR and MDTLC detection limit was, therefore, established at 0.1 parts per

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Figure 4. Scheme for resolution of MeCl$_2$ extract of CW3 by MDTLC

Table 6. Mass and infrared spectral characteristics of MDTLC separated components from the MeCl$_2$ extracts of CW3

MDTLC band*	Mass, m/e	IR, cm^{-1}	Comments
X	–	–	Insufficient quantity for characterization
XA	149, 167, 279	2925, 1730, 1380, 1290	Data indicated the presence of dibutyl phthalate, di-n-octyl phthalate and/or di-z-ethyl hexyl phthalate
XB1	–	identified as 2,4-DNT	
XB2	–	identified as 3-amino 2,4-DNT	
XB3A	180, 197	2925, 1730, 1380, 1290	IR spectrum obscured by contaminants m/e 197 suggested an amino DNT cpd.
XB3B	149, 156, 165, 167, 180, 185, 197	2925, 1730, 1380, 1290	Data indicated phthalates, m/e suggested an amino DNT cpd.
XB4	156, 180, 197	2925, 1730, 1380	IR spectrum obscurred by DBP ME 197 suggested an amino DNT cpd.
XB5	149, masses attributed to C$_n$H$_{2n-1}$ ion series	2925, 1730, 1380	All data indicated presence of of phthalates.
XC1	same as XB5	2925, 1730, 1460, 1380, 1240	Same as XB5
XC2A1	same as XB5	2925, 1730, 1540, 1380, 1240	Same as XB5
XC2A2	183, 197, 208	2925, 1538, 1380, 1340	m/e 97 suggested amino DNT cpd. Ill defined IR spectrum
XC2A3		identified as 4-amino 2,6-DNT	
XC2A4	same as XB5	same as XB5	Same as XB5
XC2A5			Insufficient quantity for characterization

Table 6. (cont)

MDTLC band*	Mass, m/e	IR, cm⁻¹	Comments
XC2C	149, 163, 177, 180,194, 197, 211, 223, 279	2925, 1735, 1380	m/e 149 and 279 suggested di-butylphalates, m/e 163, 194 suggested dimethylpthalate, m/e 197 suggested an amino DNT cpd. IR obscured by phthalate impurities.
XC2B			Insufficient quantity for characterization.
XC2D	149, 167, 279	2925, 1730, 1530, 1380, 1350	Nitro cpd. mixed with dibutyl phthalate, di-n-octyl phthalate and/or di-2-ethyl hexyl phthalate
XC3	149, 163, 167, 185	same as XC2D	Masses attributable to ion species other than phthalates. IR indicative of nitro cpds.
XD1			IR spectrum obscured by contaminants.
XD2		identified as 5-amino 2,4-DNT	
XD3		identified as 5-amino 2,4-DNT	
XD4	87, 129, 149, 163, 167, 180, 183, 185, 197, 213	2925, 1730, 1535, 1380, 840	All data indicated presence of phthalates M/e 163, 180, and 197 suggest amino DNT cpd. and IR suggested nitro cpds.
XD5			No data obtained
XE			Unresolved IR bands

*Refer to figure 4

million for 6 L of CW3. Thus we could detect the presence of a compound at the parts per trillion level with MDTLC, but for identification by IR, the limit would be at the 0.1 parts per million level. Combining MS with MDTLC lowered the detection level to 2 ppb for the 6 L, since a good MS spectrum could be obtained with 1 µg of separated material. This limit allows for the discussed losses.

Under optimum conditions, the MS technique identifies compounds at the 2 parts per billion level. However, when working with material recovered from silica gel plates, there is danger of the silica gel contributing its impurities to the separated material during the recovery (extraction) stage. This phenomenon was encountered with the set of plates used for the MDTLC characterization of CW3.

It was during the accumulation of IR and mass spectral data for the CW3 sample that the presence of contaminants in many of the separated components became evident. As indicated in table 6, the contaminants exhibited, in all cases, IR absorption bands at frequencies of 2925, 1730, and 1380 cm^{-1}. These bands were most intense when the amount of the separated components were at trace levels making identification impossible. Mass spectral data indicated the contaminants to be phthalates. Infrared spectral data supported this identification by the 2925 and 1730 cm^{-1} absorption bands (ref 3). The contaminants were probably absorbed from the laboratory atmosphere by the TLC plates used for the separations.

Normally, the TLC plates are washed or conditioned with acetone prior to their being spotted or streaked, as described in the Experimental section. It had been previously determined that one acetone pass was sufficient for the removal of acetone soluble impurities from the TLC silica gel. Figure 5 shows the IR spectrum of the acetone extract of silica gel removed from a TLC plate that has been normally conditioned. This spectrum shows only two definite indications of contamination, weak bands in the 2900 cm^{-1} region probably due to small quantities of hydrocarbons, and an unknown band of medium intensity in the 1380^{-1} region. The 1380 cm^{-1} band suggests nitrate ion but the concomitant nitrate band in the 800 cm^{-1} region is lacking. Fortunately, this contamination did not interfere when the identification work was done with relatively large quantities of separated unknowns. However, it did prove troublesome when the separated unknowns were at the lower limit of detectability. Repeated runs conclusively showed that this contamination was intrinsic to the silica gel. Repeated washings with acetone did not remove it. Since the plates generally used for TLC normally gave the type of blank shown in figure 5, there was no reason to suspect the presence of a phthalate after a normal acetone wash or to run IR examinations of acetone extracts of every blank plate.

After the time-consuming MDTLC characterization of the CW3 organic phase and the discovery of the phthalate contaminants, the TLC plates were examined to determine why the normal acetone wash did not remove the phthalates. Figure 6 shows an IR spectrum of the acetone extract of a TLC plate used during the characterization, prior to acetone wash. There was no doubt as to the presence of phthalates. Figure 7 shows the spectrum of the acetone extract after the TLC plate had been washed with 3 portions of acetone. The quantity of contaminant was reduced but not completely eliminated. Undoubtedly the one acetone pass was insufficient for removal of the contaminant. However, in spite of the contamination, it was possible to obtain indications of the types of compounds present in some of the separated TLC bands.

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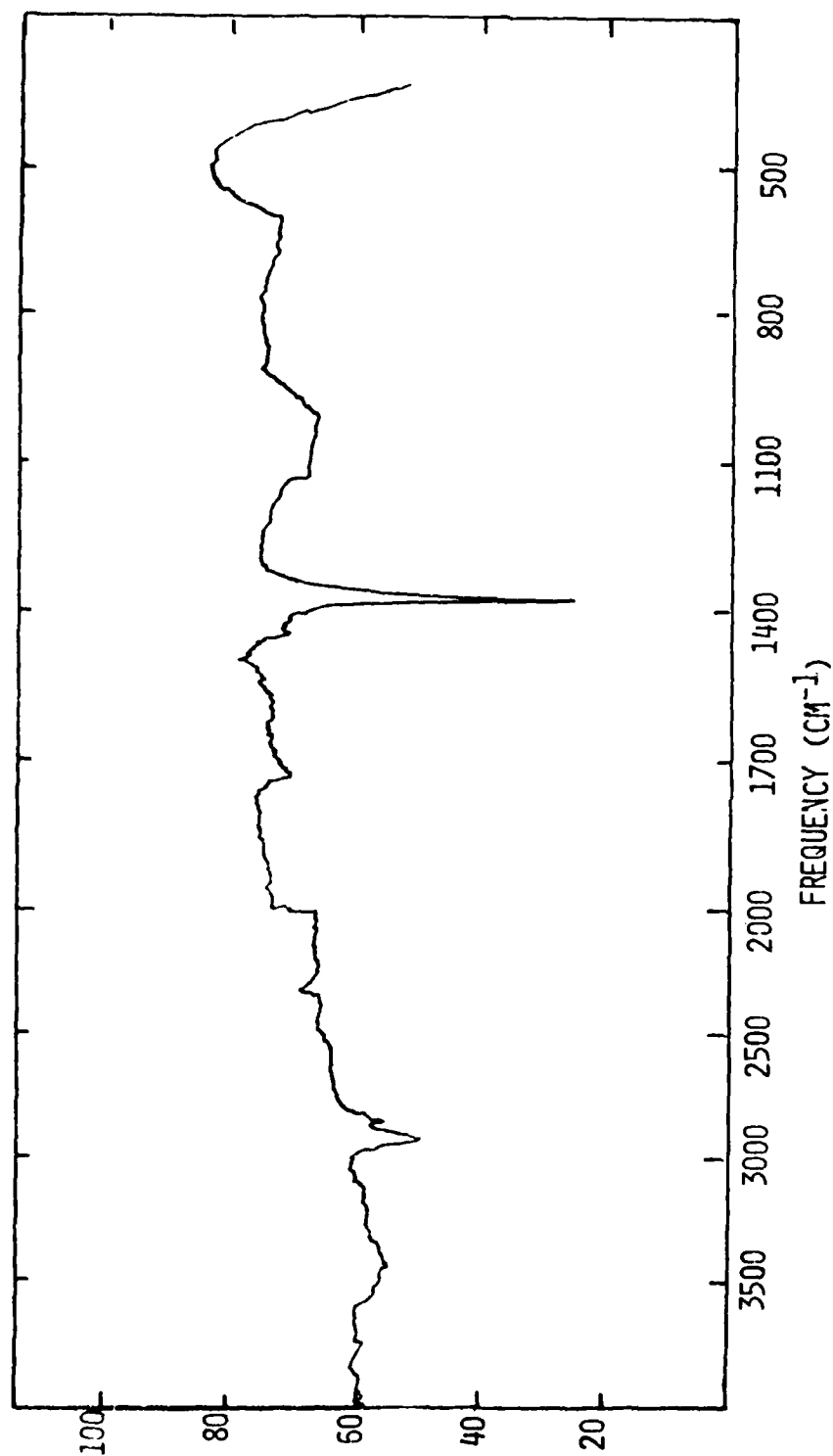
Figure 5. Normal IR spectrum blank for thin layer plate. Spectrum of acetone extract of silica gel from TLC plate prewashed with acetone
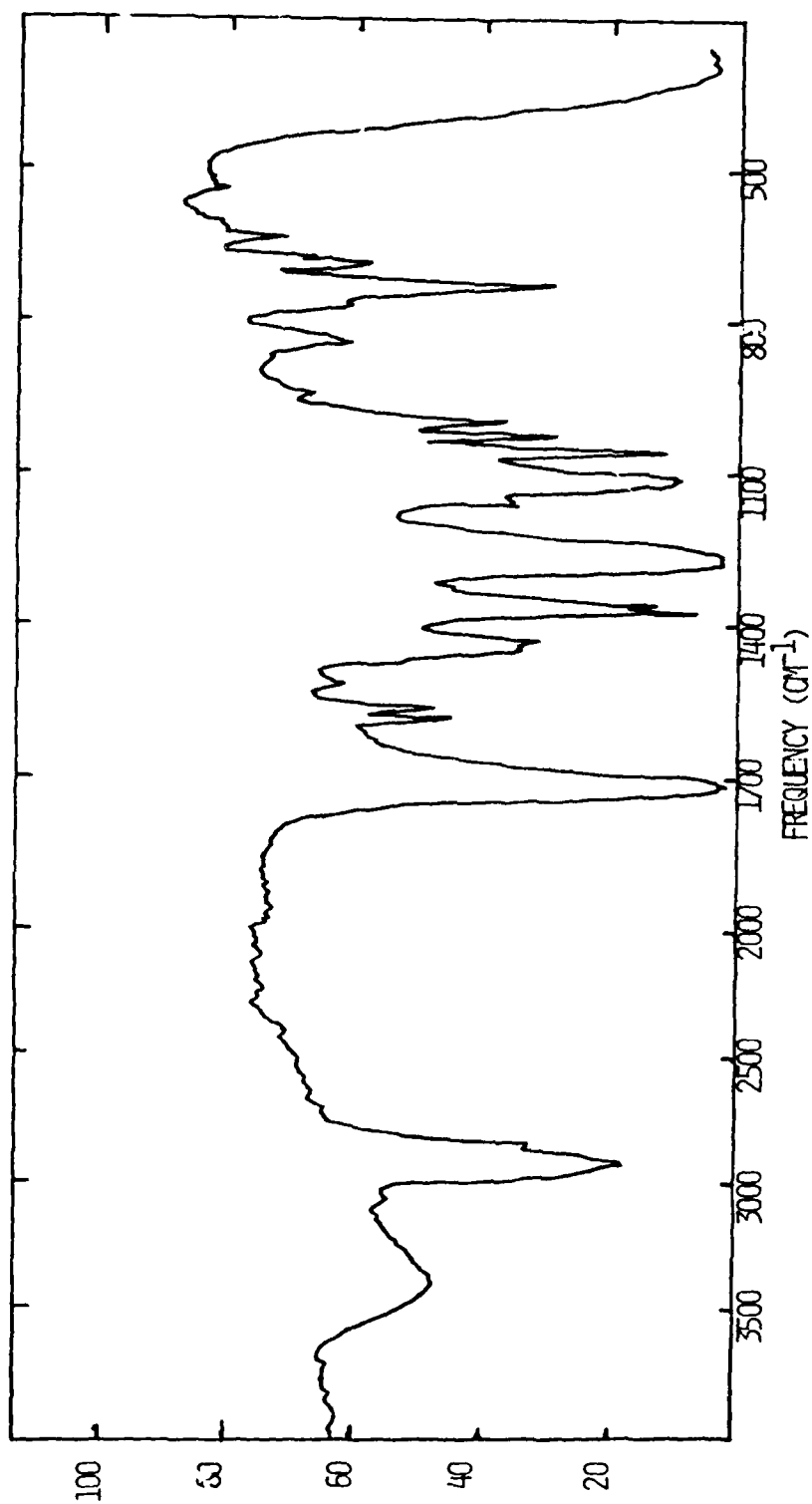
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Figure 6. IR spectrum of acetone extract of silica gel from thin layer plates used in the initial characterization of CW3
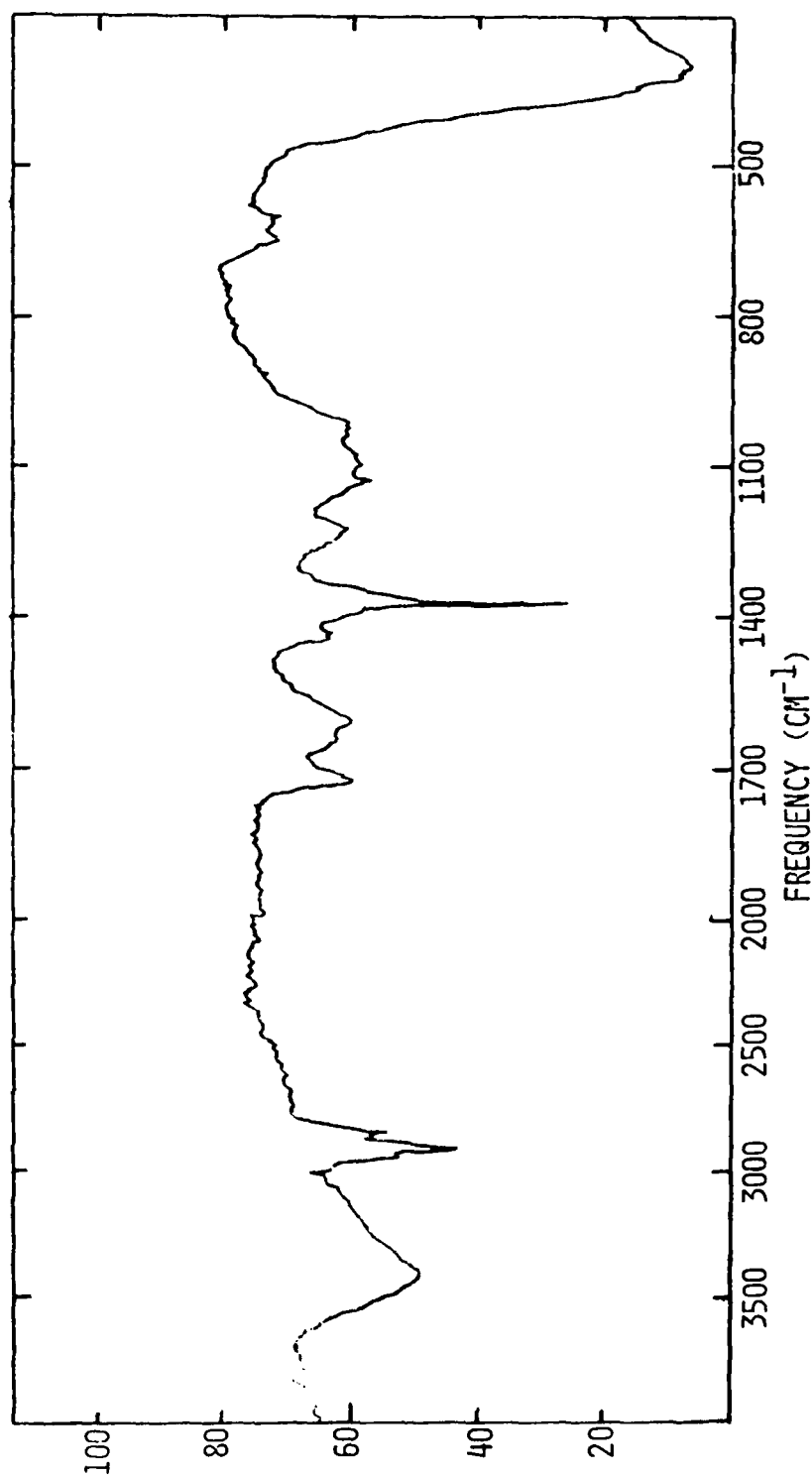
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Figure 7. IR spectrum blank of thin layer used in initial characterization of CW3. Spectrum of acetone extract of silica gel from thin layer plates after 3 acetone washes.

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Amino-dinitrotoluene (DNT) compounds seemed to be present in TLC bands XB3A, XB3B, XB4, XC2A2, XC2C, and XD4; nitrocompounds seemed to be present in XB5, XC1, and XC2A1 (fig. 4). Fresh TLC plates were used for the MDTLC characterization of the remaining sample waters. The interference from contaminants in these TLC plates was greatly minimized but not entirely eliminated.

The initial separation of the $MeCl_2$ extract from 40 L of RWC 4/14/77, outlined in figure 8, resulted in at least 34 separated TLC bands, of which 12 yielded enough material for possible identification. Amounts obtained from the remaining separated bands were considered to be less than 1 part per billion. Further resolution yielded additional bands amounting to a final total of 48 bands. Although 48 distinct bands were resolved, isolation and subsequent identification was possible for only a few compounds.

Referring to figure 8, bands A1, B1, and C1 afforded insignificant quantities of the separated components. No further effort was expended toward the resolution of these TLC bands. Components isolated from bands B4B and C2C were positively identified by IR as 4-amino 2,6-DNT, and 5-amino 2,4-DNT, respectively. These two compounds are considered to be the major components of the original extract. Similarly, bands B3C and B4A were found by IR to contain amino-nitro-compounds, although the exact isomeric forms could not be determined because of lack of reference spectra. The IR spectra of components in bands B2B, C2B, and C3B showed the presence of nitro groups and absence of amino groups. Zone A2A contains a component which IR suggests is an aliphatic hydroxy acid. Quantities recovered from bands B4A, C3B, and A4B did not afford the well defined representative IR spectra needed for positive identification by IR. Table 7 shows a summary of the results of MS examination of some MDTLC fractions from this extract.

The TLC separation of the $MeCl_2$ extract of 12 L of water from Pond Water 5 (PW5) is shown in figure 9. At least 30 separate bands were obtained, and when the silical gel containing these bands were scraped from the TLC plates and eluted with acetone, 16 of them gave enough residue to be seen in the beakers in which they were collected. These 16 components were examined by MS and 6 were identified. The mass spectra of the other 10 components were so weak that they were obscured by impurities from the silical gel. Table 8 shows the results of IR and MS examination of these separated TLC fractions. The identification of 4-amino 2,6-DNT at two different TLC plate locations cannot be explained, except that this identification represents the best guess from the mass spectral data for PW5E2.

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Table 7. Summary of mass spectrometric identification of some MDTLC bands obtained from the MeCl$_2$ extract of RWC 4/14/77

TLC band no.[a]	Most probable nitroaromatic compound present[b]	Associated major mass peaks (m/e)
B4B	4-amino 2,6-DNT	104, 180, 197
B2C	2-nitro 3-methylamino-m-xylene 4-amino 2,6-DNT	180, 163, 197
B4A	4-amino 2,6-DNT	78, 162, 163, 180, 197
B4C	4-amino 2,6-DNT	163, 180, 197
C2B	2-hydroxy 4,6-DNT	149, 181, 198
C3A	2-hydroxy 4,6-DNT	149, 181, 198
A2C	meta-or para-nitrotoluene	137
B3D	4-amino 2,6-DNT	163, 180, 197
C2C	5-amino 2,4-DNT 2,6-diamino 4-nitrotoluene	167, 180, 197 121, 167
B3A	2,6-diamino 4-nitrotoluene	121, 167
B3C	4-amino 2,6 DNT 2,4,6-TNT	163, 180, 197 210
C3C	2-hydroxy 4,6-DNT	163, 180, 197
C3D3	4-amino 2,6-DNT 2,4-diamino 6-nitrotoluene trinitrobenzene	163, 181, 198 171, 167 213
C3D8A	2,6-diamino 4-nitrotoluene	167
C3D8C	2-hydroxy 4,6-DNT	163, 181, 198

[a] Refer to figure 8
[b] The high background level and the nonavailability of some isomers of suggested structures always leaves some uncertainty in the identification of isomers. The compounds listed above are merely the "best guesses."

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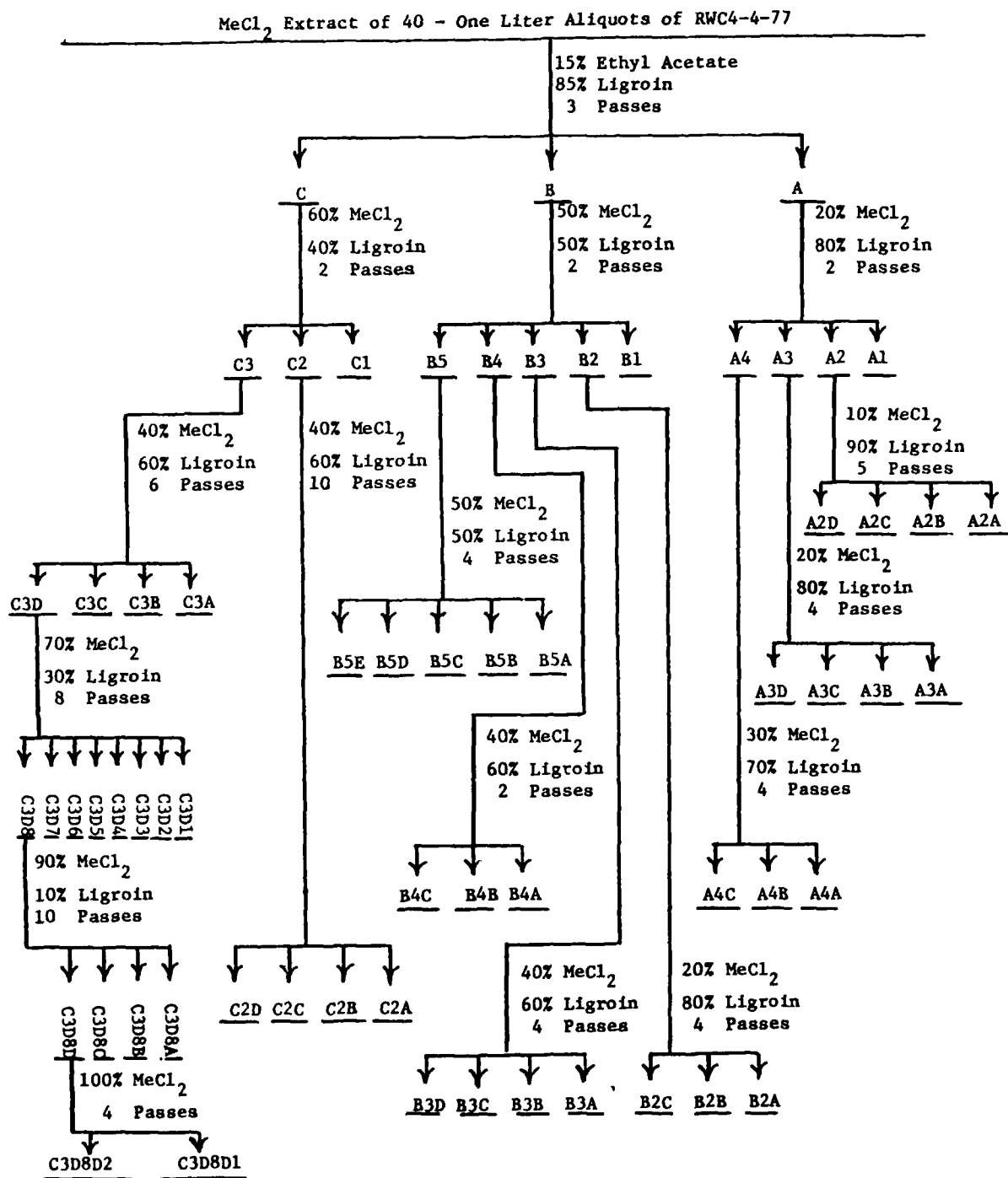
Figure 8. Resolution of MeCl$_2$ extract of RWC 4/14/77 by MDTLC

MeCl$_2$ Extract of 12-1 Liter PW-5 Samples

15% Ethyl Acetate
85% Ligroin
2 Passes

E

50% MeCl$_2$
50% Ligroin
8 Passes

D

40% MeCl$_2$
60% Ligroin
3 Passes

C

40% MeCl$_2$
60% Ligroin
8 Passes

B

30% MeCl$_2$
70% Ligroin
4 Passes

A

E7 E6 E5 E4 E3 E2 E1   D5 D4 D3 D2 D1   C3 C2 C1   B4 B3 B2 B1   A4 A3 A2 A1

70% MeCl$_2$
30% Ligroin
2 Passes

70% MeCl$_2$
30% Ligroin
9 Passes

E6C E6B ECA

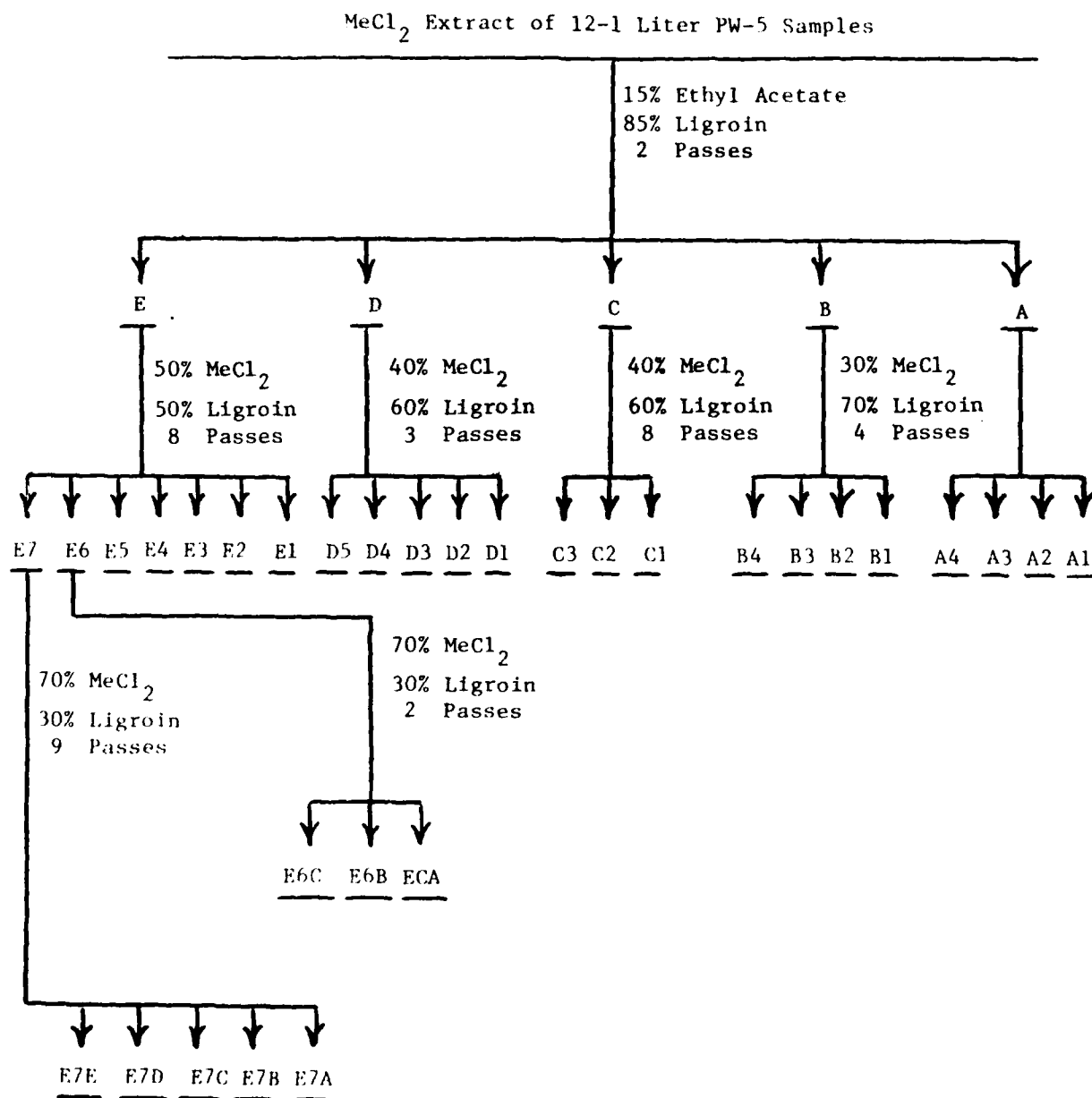E7E E7D E7C E7B E7A

Figure 9. Resolution of MeCl$_2$ extract of PW5 by MDTLC

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Table 8. Mass and infrared spectral characteristics of some MDTLC separated components from the MeCl$_2$ extract of PW5

MDTLC band*	Mass, m/e	IR, cm^{-1}	Comments
PW5-B1	148, 165, 182, 183	identified as 2,6-DNT	All data MS & IR indicate presence of 2,6-DNT
PW5-B4	137, 149, 167, 213 traces of 165, 182	-	MS data suggest the most probable cpds. present are 1,3,5 trinitrobenzene and 2,4-DNT
PW5-E2	163, 180, 197	-	4-amino 2,6-DNT as the most probable cpd. present
PW5-E3	105, 121, 134, 152, 167, 180, 197	identified as 2-amino 4,6-DNT	All data indicated presence of 2-amino 4,6-DNT
PW5-E4	163, 180, 197, 213	identified as 4-amino 2,6-DNT	All data indicated the presence of 4-amino 2,6-DNT

*See figure 9

A sample of sludge collected from the bottom of pond 5 at the plant site boundary, was air dried and extracted with MeCl$_2$. The extract was examined by TLC and its behavior found to be unusual. When the very nonpolar solvent petroleum ether was used as the developing solvent, much of the extract moved up the plate with the solvent front, indicating that a large quantity of nonpolar material was present. Sixty-two percent of the extract (918 ppm in the sludge) was found to be soluble in petroleum ether. The remainder of the MeCl$_2$ extract (562 ppm in the sludge) was found to be soluble in petroleum ether. The remainder of the MeCl$_2$ extract (562 ppm in the sludge) was separated into 23 components (fig. 10).

Gas Chromatography

The initial plan was to separate and identify the pollutants in the sample waters by MDTLC, IR, and MS techniques, and to estimate the quantities of the identified components by GC or other applicable techniques. Because of the impurity problem with the TLC plates, it was necessary to rely on GC as an adjunct technique for the reolution of the MeCl$_2$ extracts of the sample waters, aware of the possibility of the decomposition of thermally sensitive components.

MeCl$_2$ Extract of Ligroin Insolubles from PW-5 Sludges

15% Ethyl Acetate
85% Ligroin
10 Passes

B

20% MeCl$_2$
80% Ligroin
4 Passes

A

20% MeCl$_2$
80% Ligroin
4 Passes

B4   B3   B2   B1

A4   A3   A2   A1

50% MeCl$_2$
50% Ligroin
2 Passes

30% MeCl$_2$
70% Ligroin
3 Passes

B3C   B3B   B3A

A3D   A3C   A3B   A3A

60% MeCl$_2$
40% Ligroin
3 Passes

50% MeCl$_2$
50% Ligroin
2 Passes

30% MeCl$_2$
70% Ligroin
4 Passes

30% MeCl$_2$
70% Ligroin
2 Passes

B4E   B4D   B4C   B4B   B4A   B2B   B2A   A4E   A4D   A4C   A4B   A4A   A2B   A2A
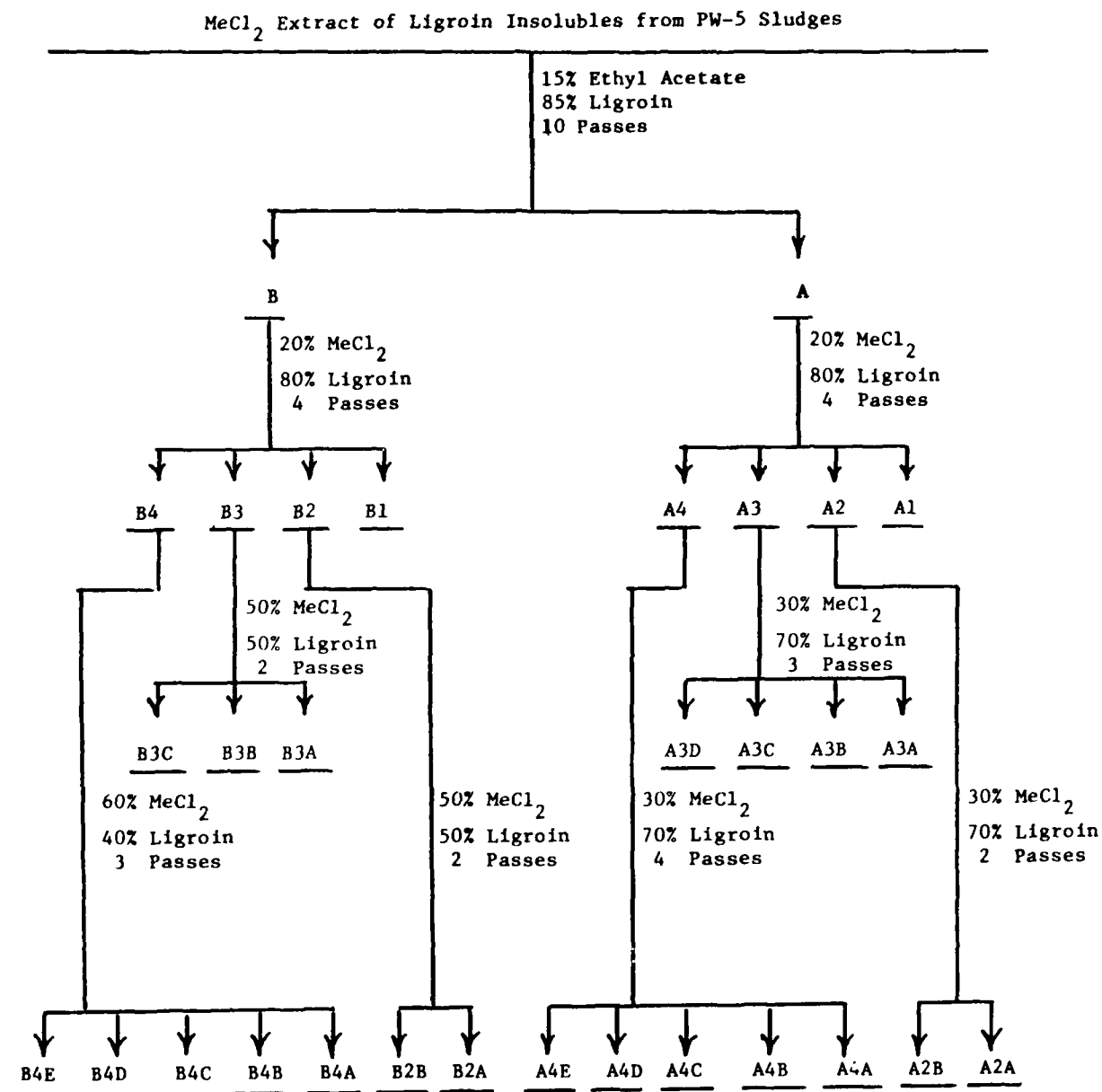
Figure 10.   Resolution of MeCl$_2$ solubles and ligroin insolubles from PW5 sludge
by MDTLC

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A GC analysis of the CW3 MeCl$_2$ extract showed at least 10 detectable peaks (fig. 11). Through the collection of the GC effluent for each peak, GC spiking, IR, and MS, practically all peak components were identified. Table 9 shows a summary of the identified compounds. An estimation of the quantities of the identified compounds done by the GC internal standard method are shown in Table 10. The 2,4-DNT, 2,6-DNT, and 3-amino-2,4-DNT were the major components identified. A total of 13.1 ppm or about 67% MeCl$_2$ extract was accounted for. The remaining components were either present in quantities less than the detection limit of the detector or not separated by the GC conditions used for the analysis.

Table 9. Identification of GC peaks of MeCl$_2$ extract of CW3

Peak number[a]	Compound	RR$_t$[b]	Mass data, m.e.[c]	Comments
1	2,6-DNT	1.75	182, 165, 148	Combination of mass data and RR$_t$ data indicated
2	m-dinitrobenzene (DNB)	1.85	168, 152	presence of 2,6-DNT and m-DNT
3	2,4-DNT	2.18	182, 165	Presence of 2,4-DNT also confirmed by MDTLC/IR[d]
4	3,5-DNT	2.27	182, 165	Combination of mass data
5	3,4-DNT			and RR$_t$ data indicated presence of 3,5- and 3,4- DNT isomers[d]
6	3-Amino 2,4- DNT	2.61	197	3-amino 2,4-DNT also confirmed by MDTLC/IR[d]
7	Amino DNT	3.21	197	Amino DNT also indicated by MDTLC/IR[d]
8	4-amino 2,6- DNT	3.45		Presence of the 4-amino 2,6-DNT
9	2-amino 4,6- DNT	4.05		2-amino 4,6-DNT and 5- amino 2,4-TNT
10	5-amino 2,4- DNT	4.57		isomers also indicated by MDTLC/IR[d]

[a]See figure 11
[b]Relative to p-mononitrotoluene
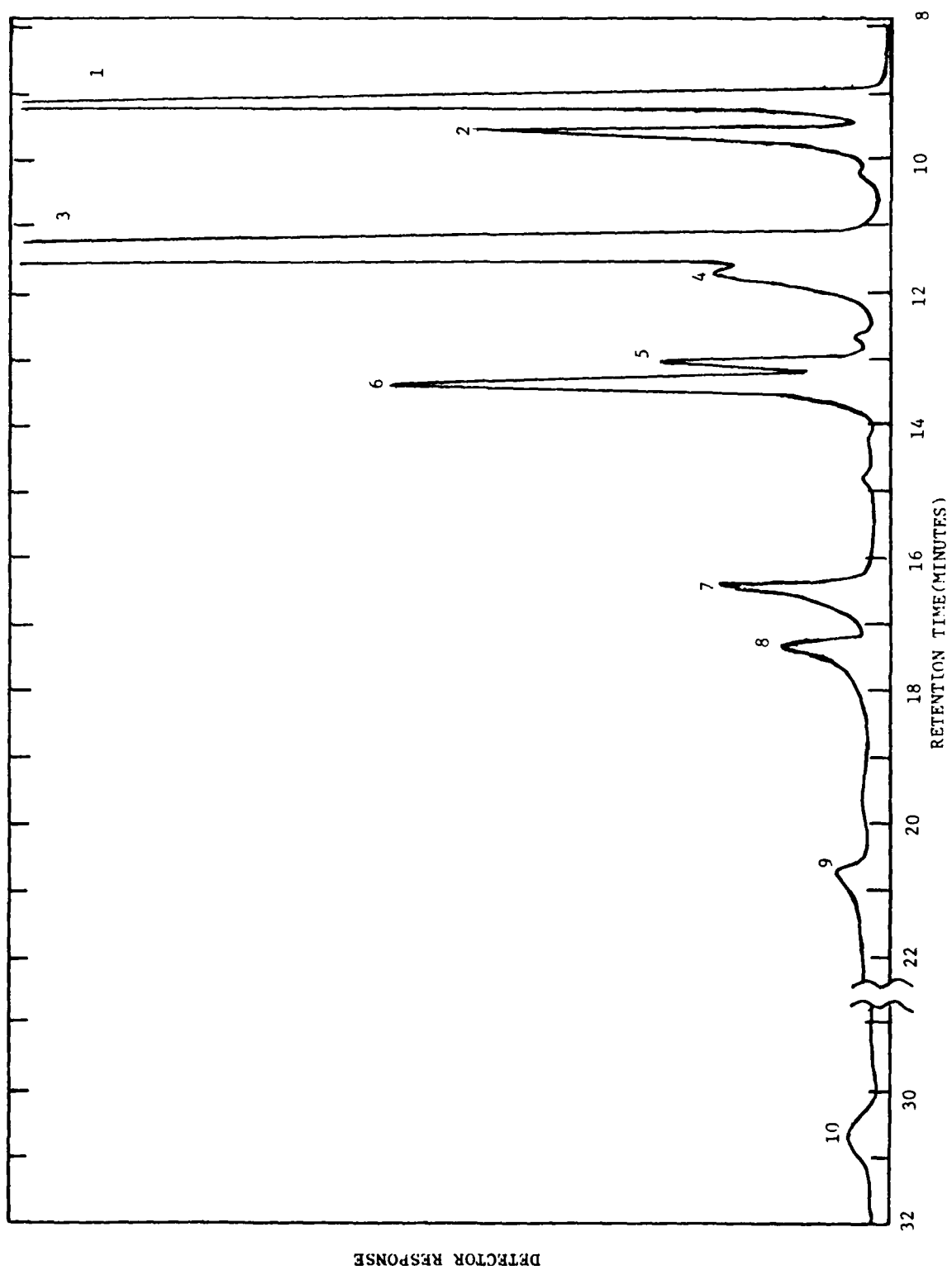[c]Samples obtained by collected GC effluents
[d]See table 6

Figure 11. Gas chromatogram of CW3 MeCl$_2$ extract

Table 10. Quantitative estimation of the identified components in MeCl$_2$ extract of CW3 as determined by GC*

Compound	Parts per million (ppm)
2,6-DNT	1.9
m-DNT	0.62
2,4-DNT	6.9
3,5-DNT	0.4
3,4-DNT	0.63
3-amino 2,4-DNT	1.0
Amino DNT	0.8
4-amino 2,6-DNT	0.4
2-amino 4,6-DNT	0.25
5-amino 2,4-DNT	0.21
Total, ppm	13.11

*Internal standard method

A sample of the MeCl$_2$ extract of condensate water RWC 4/14/77 yielded the chromatogram shown in figure 12. Since the thermal conductivity detector is less sensitive than the FID, the chromatogram shows only peaks corresponding to the major components of the MeCl$_2$ extract. Since the effluent from the chromatographic column is not decomposed in the TCD as it is in the FID, the separated components were collected at the exit port of the instrument. Significant amounts of the components could be collected by condensation at the exit port during the elution of peaks numbered 1 to 6 (except 4) on the chromatogram shown in figure 12. Repeated injections of the MeCl$_2$ extract of RWC 4/14/77 into the column of the gas chromatograph were made to collect enough of each of these six components to attempt identification. At least 20 runs were required to collect a significant amount of the low concentration components. These components were examined by MS and IR spectrophotometry, and the identifications are listed in table 11. The mass spectrum for peak number 4 was too weak for identification and not enough material was available for a well-defined IR spectrum. Attempts to identify peaks B to D were made by spiking with known compounds, identity clues given by their retention times. Tentative identification of these peaks are also shown in table 11. Peaks 4A and E could not be identified. The quantitative estimates of the identified components (table 12) were made by the usual GC normalization method. Recourse to the normalization method was made when it became difficult to obtain some of the identified materials as standards, as required by the internal standard method.
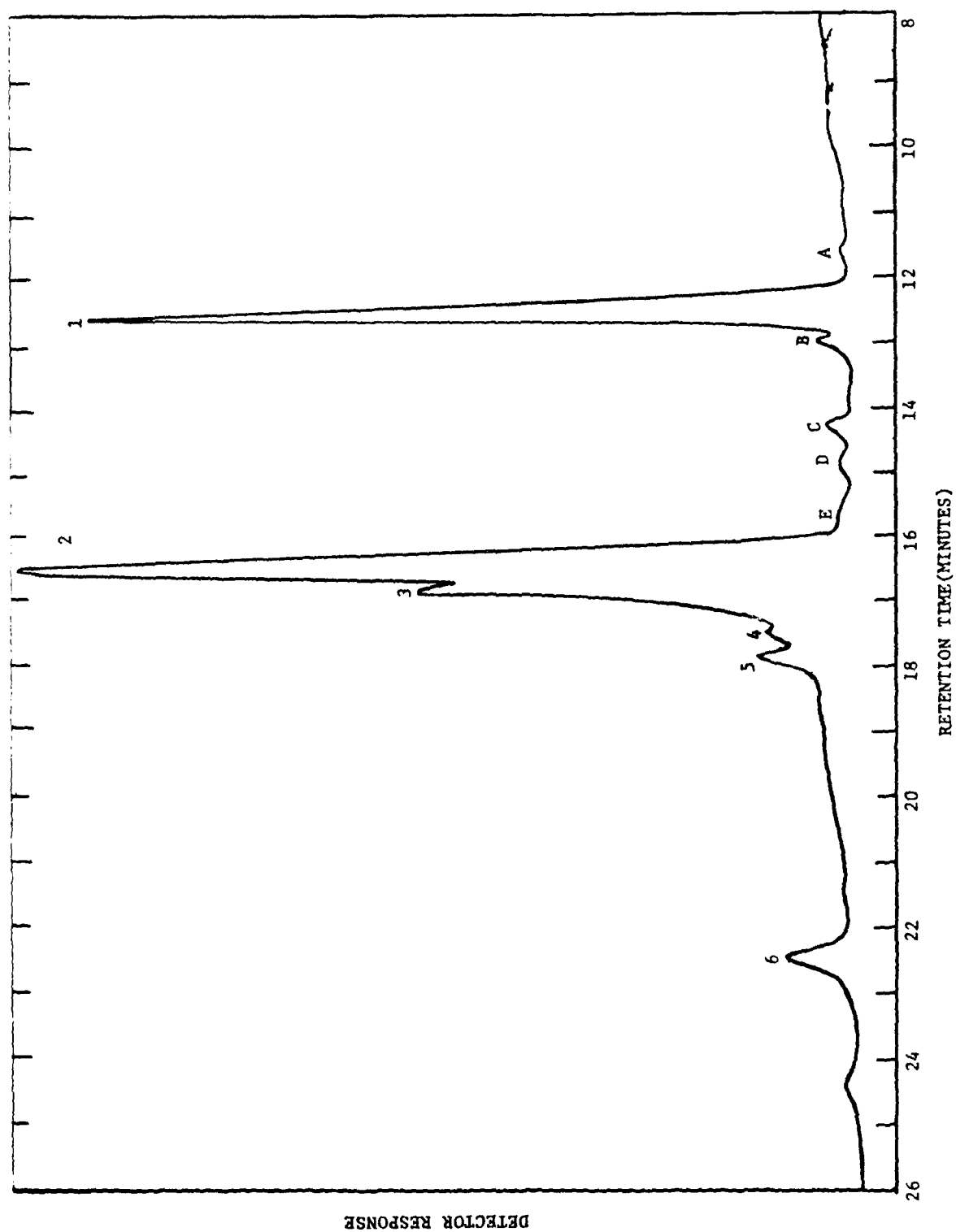
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Figure 12. Gas chromatogram of the $MeCl_2$ extract of RWC 4/14/47

Table 11. Identification of GC peaks of MeCl$_2$ extract of RWC 4/17/77

Peak designation[a]	Compound	Mass data m/e[b]	Comments
1	2,6-DNT	121, 135, 148, 165, 182	Mass spectral data indicated 2,6-DNT, confirmed by infrared[b] spectral characteristics and by GC peak spiking.
2 3	5-hydroxy 2,4-DNT 4-hydroxy 2,4-DNT 6-hydroxy 2,3-DNT or 6-hydroxy 2,4-DNT	135, 164, 181, 198	Insufficient mass spectral data made it impossible to identify which of the hydroxyl DNT isomers was present in peaks 2 and 3. DNT had also been indicated by MDTLC/mass data.[c]
5	3-amino 2,4-DNT	104, 105, 134, 135, 150, 162, 163, 180, 197	The mass spectral data indicated the 3-amino 2,4-DNT cpd.
6	6 hydroxy 2,4-DNT or 6 hydroxy 2,3-DNT	104, 105, 151, 162, 163, 168, 180, 181, 198	For reason given for peaks 2 and 3, the actual isomer could not be identified.
B C D	TNT 2,4-DNT 3,5-DNT		The sole basis for identification for these cpds were the RR$_t$ and GC peak spiking. However, TNT had been previously indicated by MDTLC/mass data.[c]

[a]See figure 12
[b]Samples obtained by collection GC effluents
[c]See table 7

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Table 12. Quantitative estimation of components in $MeCl_2$ extract of RWC 4/17/77 as determined by GC[a]

Peak number	Component	Parts per million
A	not identified	0.004
1	2,6-DNT	0.9
B	not identified	0.04
C	2,4-DNT (probable)	0.02
D	3,4-DNT (probable)	0.01
E	not identified	0.03
2	hydroxy DNT	1.5
3	hydroxy DNT	0.1
4	not identified	0.006
5	3-amino 2,4-DNT	0.03
6	6-hydroxy 2,4,- or 2,3-DNT	0.08

[a]Normalization method
[b]See figure 12 for chromatogram

The $MeCl_2$ extract of PW5 was also examined by GC using a TCD (fig. 13). Samples of the separated components represented by the nine numbered peaks were collected for identification (table 13). Four of the components, peaks 1, 5, 7, and 9, were identified by IR spectrometry and the identifications were confirmed by spiking the sample injected into the gas chromatograph with standard samples of these compounds. Peaks 4 and 6 were identified by MS. Peaks 2 and 3 were indicated to be the 2,4- and 2,5-DNT isomers by the retention times and by spiking the extract solution with the standard isomers. An estimation of the amount of each identified component (table 14) was determined by the normalization method.

Gas Chromatography/Mass Spectrometry

In conjunction with TLC-MS and collected GC eluate/MS procedures, a direct GC/MS approach, that of GC in tandem with the MS, was attempted for the first time in this laboratory. Initially the results were encouraging, leading to the quick separation and identification of a mixture of known nitroaromatics, even though the precise procedures and instrumentation needed improvement.

Figure 14 represents the gas chromatogram of the $MeCl_2$ extract of CW3. Ninety-six, 2 seconds/decade MS scans were collected during approximately 14 minutes represented by the gas chromatogram in figure 14. Figure 15 is a reconstructed chromatogram obtained by plotting the scan number (NOTE: The 96 scans are numbered 0-47-0-47 versus number of mass spectral peaks in each scan obtained from the data system scan summary). This plot should have approximated the chromatogram in figure 14 if the run conditions were satisfactory. It is apparent that figure 15 is a very poor chromatogram. This was probably due to the problems in the GC interface mentioned in the Experimental section.

Table 13.   Identification of GC peaks of MeCl$_2$ extract of PW5

Peak number[a]	Compound	RR$_t$[b]	Mass data, m/e	Comments
1	2,6-DNT	1.99	148, 165, 182, 183	Mass spectral data indicated 2,6 confirmed by the MDTLC/IR data.[a]
2	2,4-DNT	2.39		Presence of 2,4-DNT and 3,5-DNT
3	3,5-DNT			indicated by RR$_t$.
4	3,4-DNT	2.80	136, 152, 166, 182	Mass spectral data and RR$_t$ basis for identification.
5	2,4,6-TNT	3.01	180, 193, 210, 227	Presence of 2,4,6-TNT also indicated by IR spectral data.
6	1,3, 5-TNB	3.04	167, 180, 197, 213	Presence based on mass spectral data and RR$_t$.
7	4-amino 2,6-DNT	3.92	163, 180, 197, 213	Presence of 4-amino 2,6 DNT also indicated by MDTLC/IR data.[d]
8	2,4-dinitro- aniline	4.25	107, 137, 153, 183	Mass spectral data and RR$_t$ basis for identification.
9	2-amino 4,6-DNT	4.62		2-amino 4,6-DNT identification based on MDTLC/IR data[d] and RR$_t$.

[a]See figure 12
[b]Relative to p-mononitrotoluene
[c]Samples obtained by collecting GC effluents
[d]See table 8

Table 14.   Quantitative estimation of components in the MeCl$_2$ extract of PW5 as determined by GC[a]

Peak number[b]	Component	Parts per million
1	2,6-DNT	0.76
2	2,4-DNT	0.05
3	3,5-DNT	0.10
4	3,4-DNT	0.16
5	2,4,6-TNT	0.35
6	1,3,5-TNB	0.02
7	4-amino 2,6-DNT	0.14
8	2,4-dinitroaniline (?)	0.04
9	2-amino 4,6-DNT	0.06

[a]Normalization method
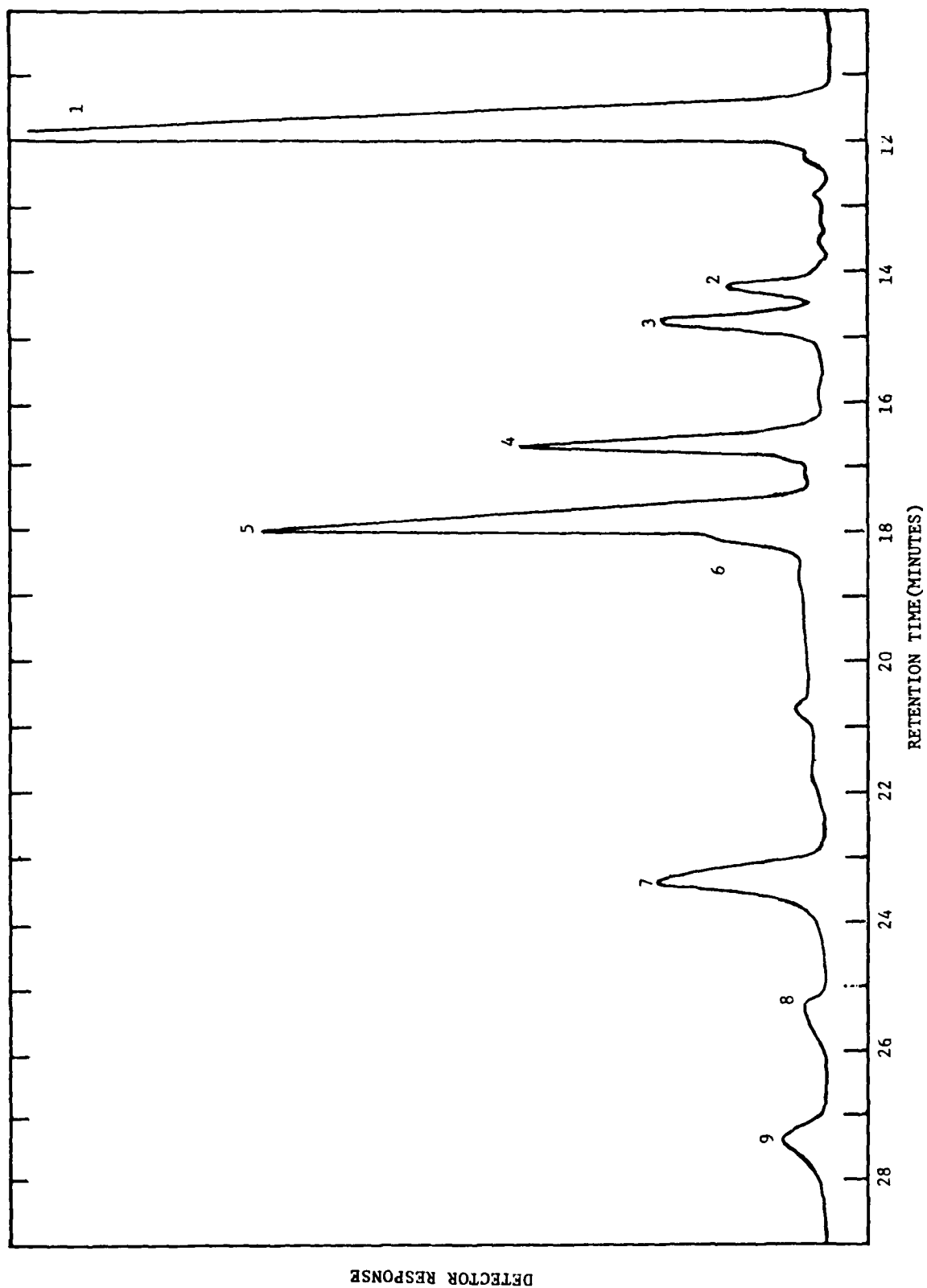[b]See figure 13 for chromatogram

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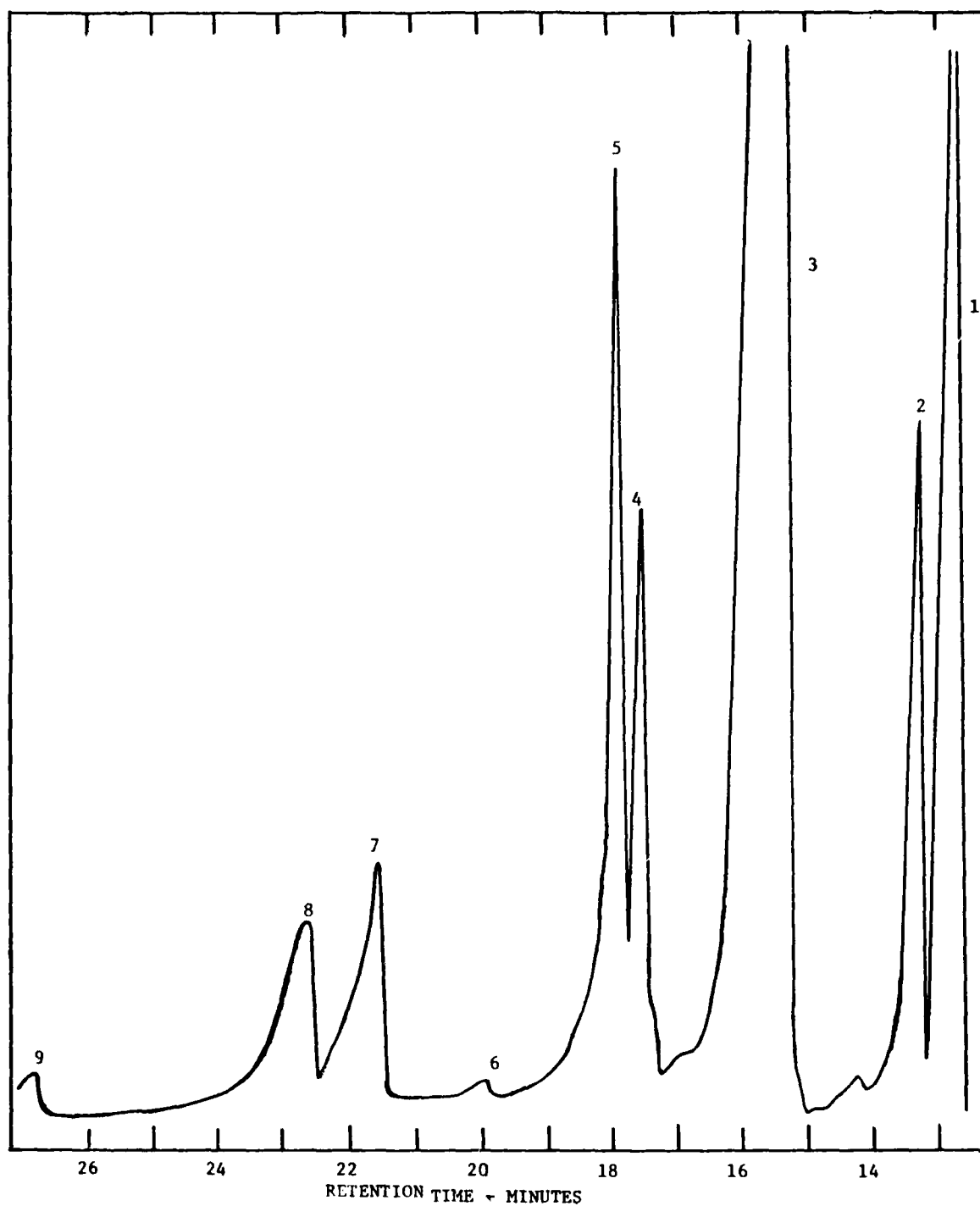Figure 13. Gas chromatogram of PW5 MeCl$_2$ extract

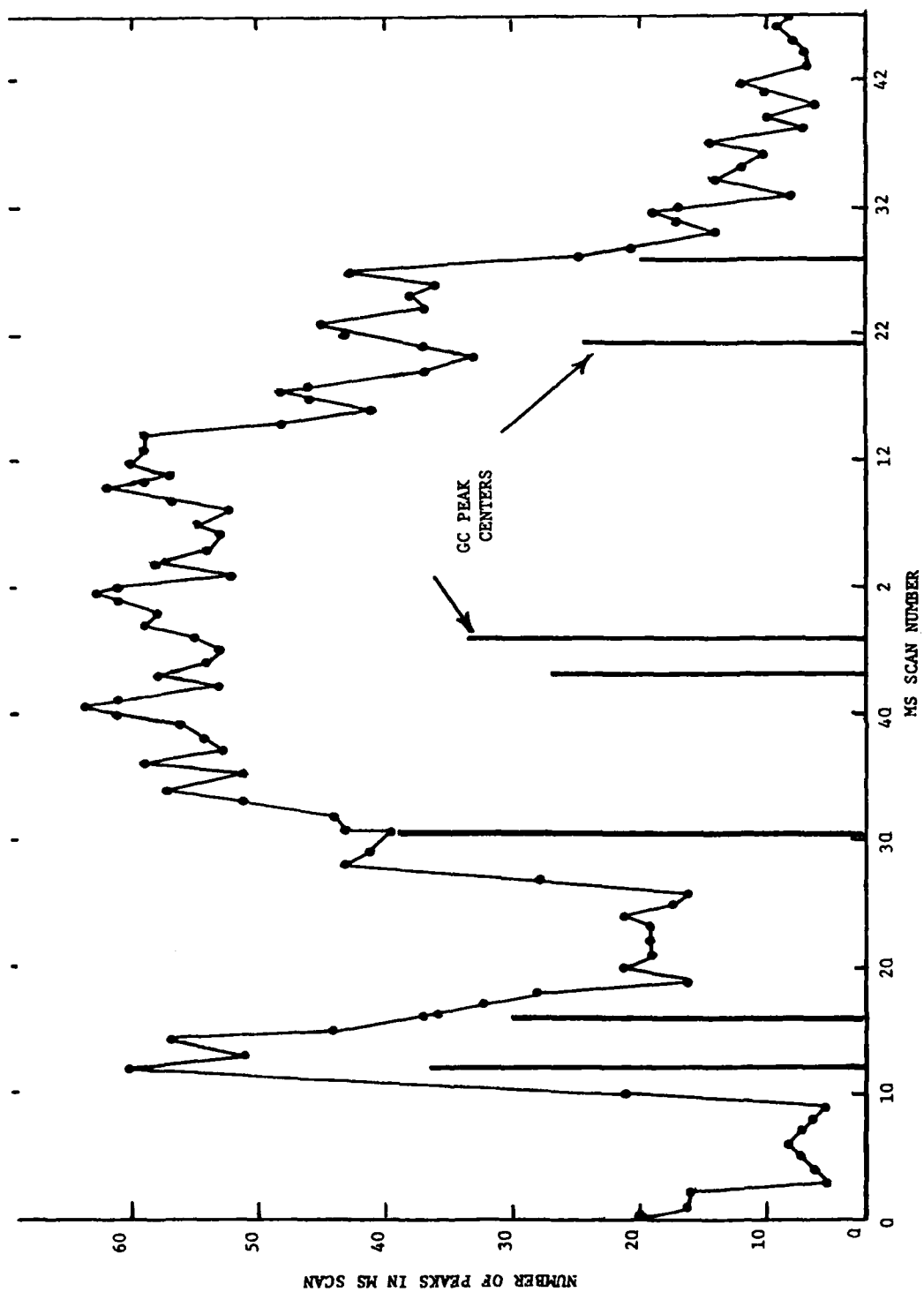Figure 14. Gas chromatogram of CW3 MeCl$_2$ extract obtained during GC/MS analysis

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Figure 15. Gas chromatogram for CW3 constructed from mass spectral scan data

Table 15 is a summary of the GC/MS analysis results for the methylene extract of CW3. It can be seen readily that there is considerable overlap in the fractions and that the quality of the mass spectra were not good enough in most cases to distinguish isomers, let alone identify unknown components.

Table 15. Summary of GC/MS (intandem) analysis of the MeCl$_2$ extract of CW3

Scan no.	Significant mass peaks	Probable origin[a]
11-13	182, 165, 148	2,6-DNT
15-17	182, 168, 165, 152, 148, 135	DNT + DNB
19	168, 152	DNB
23-24	168, 165	2,6-DNT + DNB
27-31	182, 168, 165, 152	2,4/2,5-DNT + DNB
33-36	182, 168,165	DNT + DNB
40-44	182, 165	DNT (2,4/2, 5)
46-47	182, 165	DNT (2,4/2,5)
1-5	182, 165, 179	DNT + DNX
10-15	182, 165, 196, 179	DNT + DNX
17-18	182, 165, 197, 196, 179	DNT + DNX + ADNT
22-27	196, 179, 197, 180, 165	DNT + ADNT + DNT
34	138	NA
37-42	165, 138	DNT + NA
45	106[b]	?
46	138	NA

[a]DNT = Dinitrototoluene; DNB = Dinitrobenzene; DNX = Dinitroxylene; ADNT = Ammodinitrotolune; NA = nitroaniline
[b]Questionable

The gas chromatogram of the MeCl$_2$ extract from RCW 4/14/77 is shown in figure 16. The chromatogram constructed from the mass spectral scan data (fig. 17) represents a considerable improvement over the reconstructed chromatogram for CW3 (fig. 15). The gas chromatogram for RWC 4/14/77 (fig. 16) showed 11 peaks. The two strongest GC peaks were 1 and 4. Peaks 2, 6, 7, 9, 10, and 11 were all well defined. Peak 3 was quite small, whereas peak 5 was a shoulder on the trailing edge of peak 4. There was strong tailing from peaks 9, 10, and 11. Peak 8 was a broad, low intensity peak.

Table 16 summarizes the GC/MS data for RWC 4/14/77. The scans under each GC peak were used for the identifications given in the last column. Table 16 shows that GC peaks 1 and 4 were identified as due to 2,6-DNT and 2,4-DNT, respectively. The presence of m/e 182 as the highest mass and of m/e 165 as the most abundant fragment identified a DNT (mass - 182) with at least one nitro group ortho to the methyl group. The relative abundance of fragments of lower mass allowed position
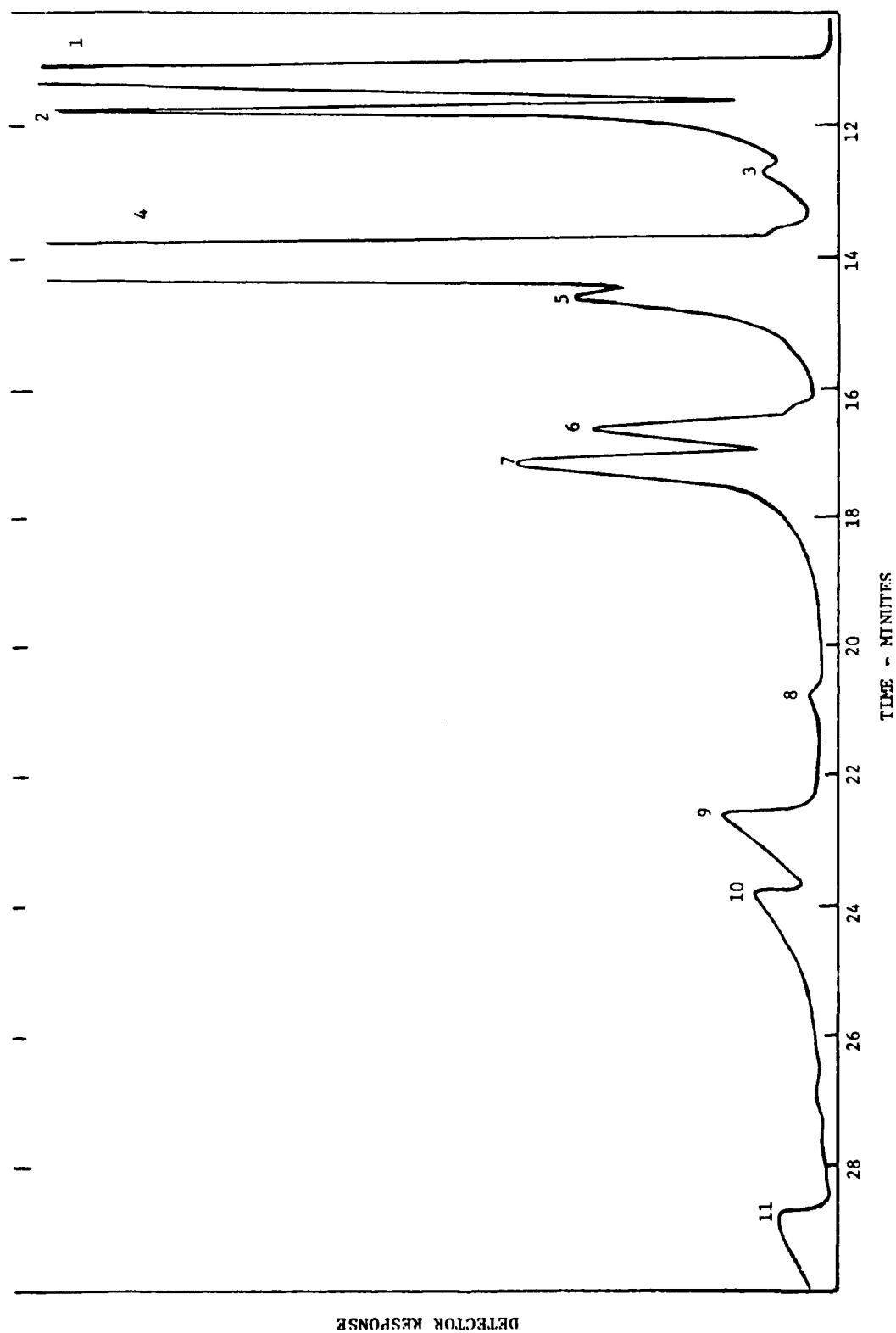
40

Figure 16. Gas chromatogram of RWC 4/14/77 MeCl$_2$ extract obtained during GC/MS analysis
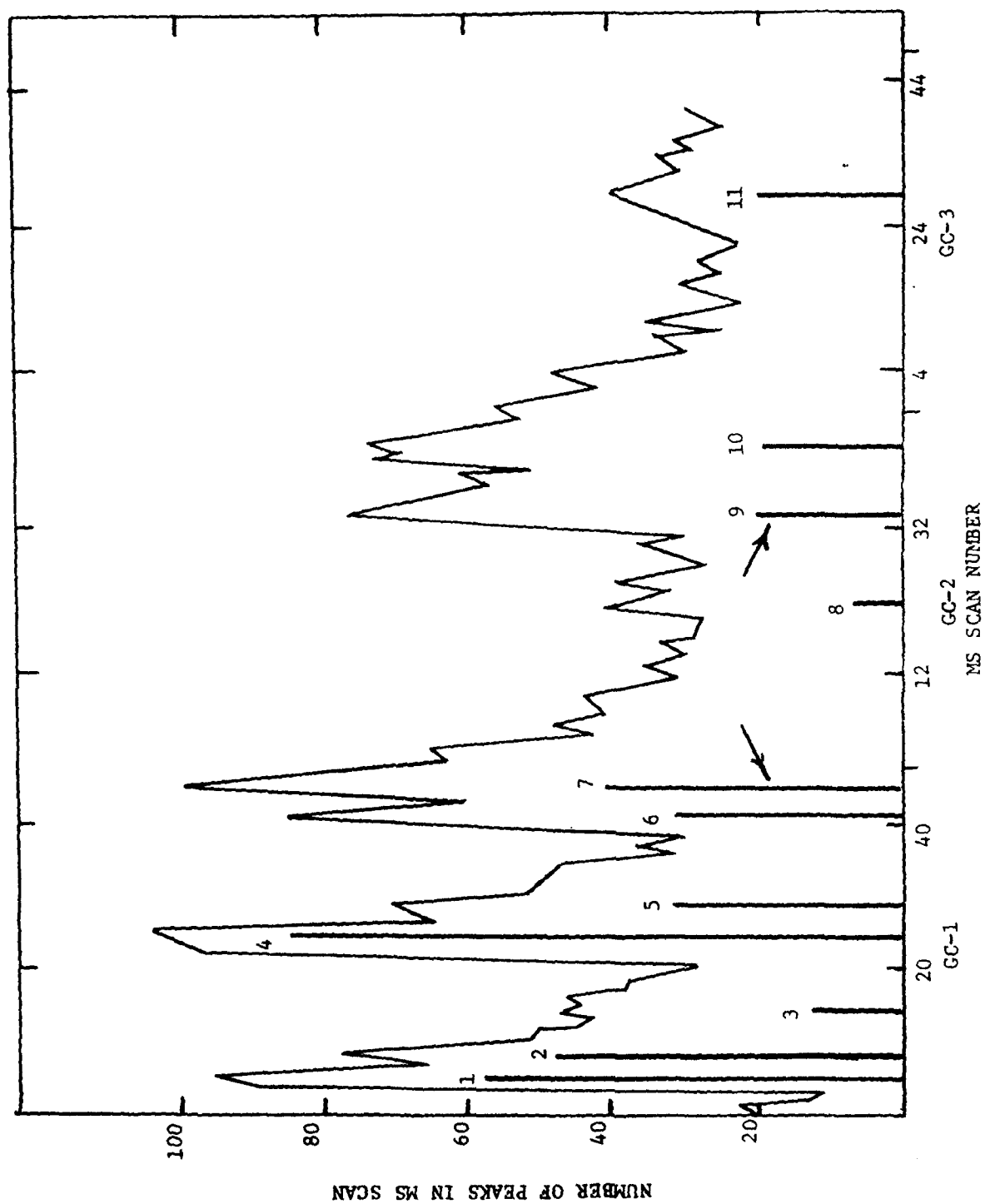
Figure 17. Gas chromatogram of RWC 4/14/77 constructed from mass spectral scan data

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identification. Gas chromatography peaks 2 and 3 were identified as due to dinitrobenzenes by the same techniques. The highest mass was m/e 168. There was a strong mass peak at m/e 165, suggesting the presence of DNT (possibly the 2,6-isomer from peak 1). The GC peak 5 was identified as due to 3,5-DNT both by the pattern of mass fragments and by the order of elution of the DNT from an SE30 column. The GC peak 6 gave a fragmentation pattern characteristic of a dinitroxylene (m/e 196) with some admixture of a DNT. The isomers could not be identified. The GC peaks 7, 9, 10, and 11 showed patterns characteristic of the amino-DNT's with the molecular ion at m/e 197 and the base (largest) peak at m/e 180. The isomers could not be identified due to lack of spectra of the pure substances for comparison. The GC peak 8 is almost certainly a mixture. The amount of material available to the mass spectrometer was too small to give a strong fragmentation pattern and identification was impossible. The presence of a fragment of m/e 197 would suggest an amino-DNT, for example, but the absence of a fragment of m/e 180 makes this suspect.

Table 16. Summary of GC/MS (intandem) analysis of the MeCl$_2$ extract of RWC 4/17/77

GC peak no.	Retention time, min	MS scan numbers[a]	Probable identification[b]
1	11.2	5/18 GC1 - 4,5,6	2,6-DNT
2	11.8	5/18 GC1 - 8,9	p-DNB + m-DNB
3	12.7	5/18 GC1 - 14 to 16	m-DNT + p-DNB + 2,6-DNT
4	14.1	5/18 GC1 - 22 to 25	2,4-DNT
5	14.6	5/18 GC1 - 26 to 29	3,5-DNT
6	16.6	5/18 GC1 - 39 to 41	DNmX + DNT
7	17.2	5/18 GC1 - 43 to 46	amino-DNT
8	20.8	5/18 GC2 - 19 to 24	
9	22.6	5/18 GC2 - 31 to 34	Amino-DNT
10	23.9	5/18 GC2 - 40 to 43	Amino-DNT
11	28.9	5/18 GC13 - 26 to 30	Amino-DNT

[a]Data collection under the AEI DS-30 system allows only 48 scans per run, therefore, 3 GC runs were queued and numbered 5/18 GC1, 5/18 GC2, and 5/18 GC3.

[b]DNT = dinitrotoluene, DNB = dinitrobenzene, m = meta, p = para, DNmX = dinitromethaxylene.

For sample RWC 4/14/77, the results obtained with the GC in tandem with the MS do not agree completely with those obtained with collected GC eluate/MS procedures. Since the data generated by these two procedures were obtained a year apart, the discrepancies suggest the possibility of a change in sample integrity during the long storage time. Although the GC columns used were different, the order of elution of 2,6- and 2,4-DNT's are the same for both the stationary phases. In comparing the two chromatograms (figs. 12, 16) (tables 11, 16) it was found that 2,6-DNT was identified as one of the two major peaks in both chromatograms. However, the chromatograms differed with respect to the identity of the second major

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peak. Initially, in the tandem GC/MS procedure, the second major peak was identified as 2,4-DNT but in the later eluate run, it was identified as hydroxy DNT. The MS data, in both instances, strongly supported the identification of these two compounds for the two different storage periods. Obviously, storage of the sample affected the integrity of the sample to the extent that composition changes occurred even though the identity of the other major component did not change. It is planned to make a study of the effect of storage time on sample composition.

Liquid Chromatograpy of Volatile Components

Liquid chromatography indicates that 2,4-DNT is the major volatile, UV absorbing pollutant in CW3. The chromatograms in figure 18 show that the same major peak occurs in the as received sample and in the sample fractionated from CW3 brought to pH 12 with NaOH (basic CW3). This peak was identified as due to 2,4-DNT by spiking the sample fractionated from basic CW3 with 2,4-DNT. The chromatogram of the as received sample suggests the presence of other DNT isomers, 2,4,6-TNT, and various mononitrotoluenes (MNT). However, the chromatogram of the fractionated sample shows that minor pollutants, particularly those which eluted after 2,4-DNT were tentatively identified as MNT's by the retention time, did not survive the treatment with strong alkali and the subsequent fractionation process.

Inorganic Phase

Samples of condensate (CW1, 2, 3, and 4) service water (SW), liquid waste treatment plant (LC PT/W-1,2) and discharge (4/30/77, 8/17/76, 8/20-23/66, 9/03/76, and 9/25/76) waters were analyzed for their inorganic components. The result of the spark source mass spectrometric, AA, and wet chemical analyses of the samples are shown in tables 3 and 4. The SW into the plant is of good quality and potable (table 3). Many inorganic components found in the plant discharge water (table 4) fail to comply with the Federal Environment Pollution Standard and Tennessee State Pollution Standards as noted in table 17. Some of these components are manganese, chromium, lead, phosphorus, copper, nitrate-nitrite, phenol, and possibly organic nitrogen.

It is apparent that, in the manufacture of TNT at the VAAP, a great deal of the inorganic pollution arises from the stainless steel nitration vessels and holding tanks. It is quite fortunate that the water is made sufficiently alkaline so that most of these elements hydrolyze and precipitate. Nevertheless, continued studies must be maintained in order to determine if these hydrolyzed elements are chelated by TNT or its degradation products. For example, phenol derivatives can chelate magnesium, zinc, and lead. The effects of these reaction products on the body may be cumulative and disastrous, such as was found to be the case with the chelate, dimethyl mercury. Until a few years ago, it was always assumed that mercury in waste waters would simply be reduced to metal and lie at the bottom of a sump awaiting removal and not react with other wastes to form a biologically active material. In view of the unknown biochemical reactions of some of these trace metals, and the nitrobodies present in the water, the effluents must be continuously

| Type Analyses | Federal Regulations EPA PERMIT NO. TN0002313 | | | Tennessee State Regulations | | | Compliance | |
	Daily Avg (lbs/day)	Daily Avg (Mg/L)	Daily Max (Mg/L)	Daily Avg (Mg/L)	Daily Max Mg/L Instantaneous Max	Total Daily Max (lbs/day)	State	EPA
Flow M³/Day(MGD)	N/A	N/A	N/A	---	22.5	---	Yes	---
Ammonia (as N)	---	0.1	0.5	0.5	1.0	94	No	No
BOD₅	66	---	10.0	10	15	1,885	No	No
COD	---	---	20.0	---	---	---	---	No
Chromium (Total)	0.33	---	0.05	0.05	0.075	9.4	No	No
Copper	0.13	---	0.02	0.02	0.03	3.8	No	No
Dissolved Solids	---	750	1000	500	750	94,240	No	No
Iron	---	---	0.3	0.3	0.45	56.5	Yes	Yes
Lead	0.33	---	0.05	0.05	0.075	9.4	Yes	Yes
Manganese	---	---	0.05	0.05	0.075	9.4	No	No
Mercury	.013	0.002	.005	0.005	0.0075	0.94	Yes	Yes
Nitrate & Nitrite	---	---	10	10	15	1,885	No	No
Oil & Grease	99	10	15	30	40	5,655	No	No
Phenol	0.0066	---	.001	.001	.002	0.19	Yes	No
Phosphate(Phosphorus)	---	---	0.1	0.1	0.15	18.8	No	Yes
Settleable Solids	---	---	0.5 ml/l	0.5 ml/l	---	---	Yes	Yes
Sulphate	---	---	250.0	250	500	47,120	No	No
Suspended Solids	---	30	---	40	50	7,539	Yes	Yes
TNT & Nitrobodies	---	0.3	0.5	0.5	0.75	94	No	No
Temperature	---	---	32.2°C	---	---	30.5°C	Yes	Yes
pH	6.5-8.5	---	---	---	---	---	Not 100%	Yes
Dissolved Oxygen	N/A	N/A	N/A	5.0 or>5.0	---	---	Yes	Yes
Residual Chlorine	N/A	N/A	N/A	0.1	0.2	18.9	Yes	Yes
Total Nitrogen(TKN)	N/A	N/A	N/A	20	30	3,770	To be Tested	Yes
Color, Odor, Taste, Scum	N/A	N/A	N/A	None	---	---	Yes	Yes

Daily Max (lbs/day) not applicable (N/A)

Table 17. Existing applicable water pollution standards – effective 1 October 1974

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Figure 18.   Liquid chromatograms of CW3
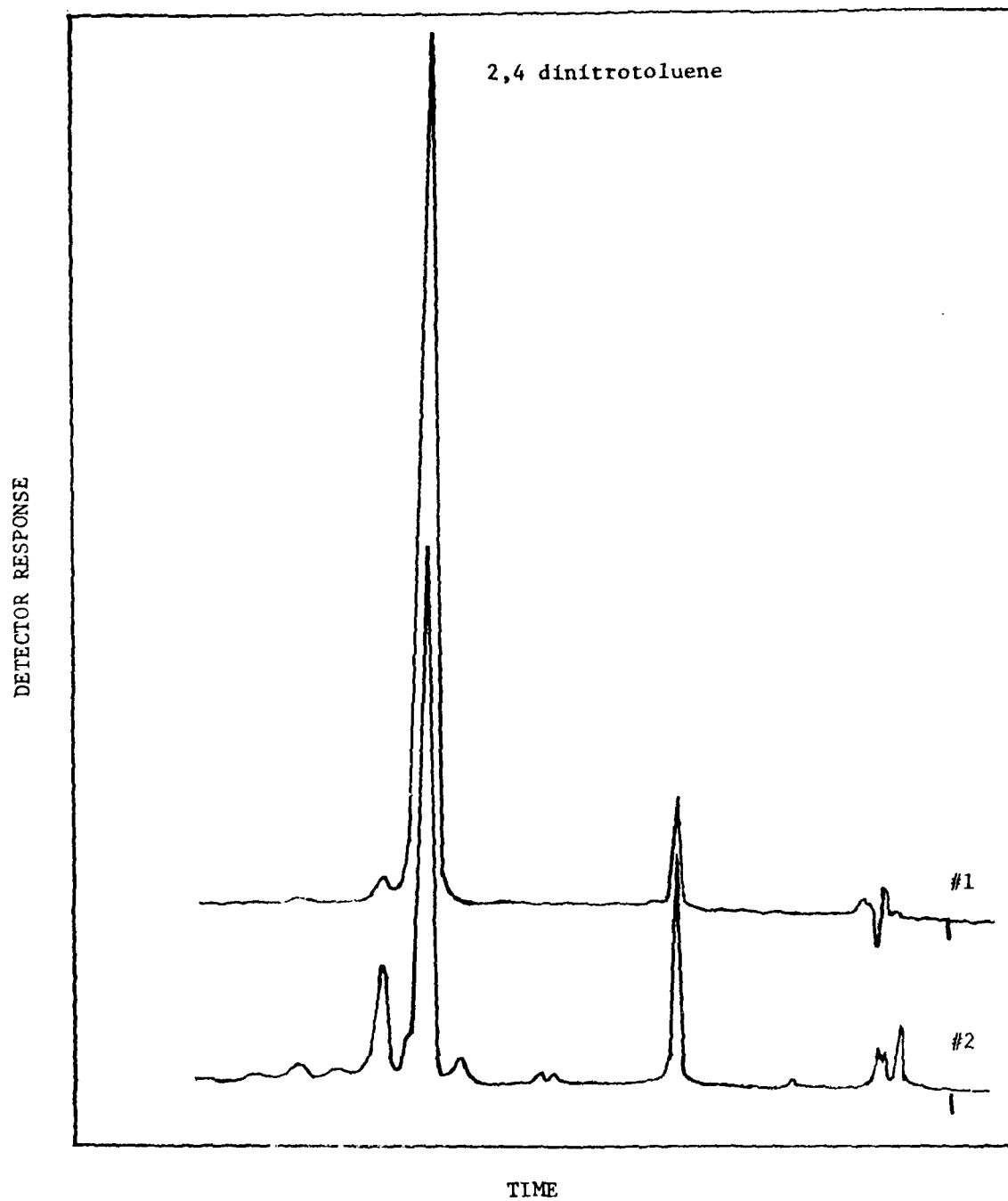
#1 - Sample fractionated from basic solution and then spiked with 2,4 DNT.
#2 - "As received" sample.

monitored and further toxicological studies undertaken to assure that the waste water effluents discharged into public waters meet EPA standards.

CONCLUSIONS

The VAAP condensate water, originating from the TNT manufacturing process, contain 30 or more organic compounds at the parts per million or lower. The DNT's, TNB, amino- and hydroxy-DNT's appear to be the major trace organics.

Evidence was found for the effect of storage time on the nature of the organics in the condensate water.

Water discharged into public water during the time that the samples for this study were collected did not meet either federal or state pollution standards.

Further evaluation and standardization of analytical techniques for the characterization of army ammunition plant waste waters is indicated.

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GLOSSARY OF ABBREVIATIONS USED IN TEXT, TABLES, AND FIGURES

AA	atomic absorption
AEI	Associated Electrical Industries
AFS	ampere full scale
CW3	condensate water sample no. 3
DNB	dinitrobenzene
DNT	dinitrotoluene
FI	flame ionization
FID	flame ionization detector
GC	gas chromatography
GS/MS	gas chromatography/mass spectrometry
IR	irfrared
LC	liquid chromatography
LWTPW	liquid waste treatement plant water
MS	mass spectrometry
MeCl$_2$	methylene chloride
MNT	mononitrotoluene
MDTLC	multi development thin layer chromatography
PW	pond water
RWC	red water condensate
SW	service water
TCD	thermal conductivity detector
TLC	thin layer chromatography
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
UV	ultraviolet
VAAP	Volunteer Army Ammunition Plant

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